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NOTE.

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Contents.

The Effect of Sulphates on the Melting, Working and Other Properties of Potash-Lead Glass.

Report by the Department of Glass Technology, University of Sheffield, on Investigations carried out on behalf of the Glass Research Association.

IN some branches of glass manufacture, alkaline and other sulphates serve as raw materials. The use of saltcake as the source wholly or partially of the alkaline constituent of window glass and bottle glass is well known, and its influence is a matter of fairly common knowledge. In cases where it is used unmixed with any reducing agent, it is apt to form a thick floating layer, only comparatively slowly decomposed by the furnace gases and by the sand, and under these conditions is a source of trouble by reason of its corrosive action on the furnace walls.

Saltcake used in tank furnaces not only serves as a source of alkali but has undoubted advantages in other directions. Added to the extent of from 10 to 30 per cent. of the total alkali it tends, apparently, to assist fining operations, whilst it undoubtedly prevents the formation of the white scum, consisting mainly of silica, which is not infrequently seen on glass made wholly from soda ash.

Moreover, practical experience shows that a glass produced from saltcake has working properties somewhat different from the one where soda ash alone is the source of alkali. It is reputed, for example, in the case of window glass, to give a more durable, stronger and more readily drawn glass when cylinders are made, whilst bottle blowers aver that saltcake glass is " sweeter " than soda ash glass.

These differences may be due to more than one cause, but fundamentally are to be ascribed to the presence of small amounts of sulphate remaining undecomposed and in solution. Thus, F. Gelstharp* stated that in fifteen analyses of plate glass the percentage of sodium sulphate present varied from 0.59 to 1.74.

We have, in the Department at Sheffield, frequently found distinct amounts of SO_3 present in soda-lime glasses made in tank furnaces. Even when the glass is made from soda ash, sulphate may be present derived from furnace gases, although it is usually small in amount.

In making lead glasses, the use of sulphate is exceptional. Cases are known where substances such as plaster of Paris and strontium sulphate have been added to batches for alabaster glass.† If sulphate creeps into lead-containing glasses it may usually be ascribed to impurity either in the raw materials, or, to a minor extent, through the absorption of furnace gases.

In regard to the presence of sulphate in raw materials, this is already known as also the influence which it has in producing opalescence when present in sufficient amount. Cauwood and Turner‡ showed that sulphates, as well as chlorides, derived from Russian potash, were a likely source of trouble in lead glasses, the sulphate alone when present to the extent of 0.25 per cent. leading to opalescence in reheated or in slowly-cooled glass. These results were confirmed by Fenner and Ferguson.§

Somewhat obscure though our knowledge of the function of sulphate in the manufacture of soda-lime glass is, we know, much less of its action in the case of lead glasses.

One would like to know, for example, to what extent sulphate may be got to dissolve in such glass; whether or not it is readily decomposed. Further, whether or not it influences the rate of melting and the ease with which the glass

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* Trans. Amer. Cer. Soc., 1912, 14, 662.
† See, for example, Silvermann, J. Amer. Cer. Soc., 1918, 1, 247.
‡ J. Soc. Glass. Tech., 1917, 1, 87.
§ J. Amer. Cer. Soc., 1918, 1, 468.

may be refined. Or, again, whether there is a tendency to produce stones, either by itself or through corrosive action on the pot.

As a step towards increasing our information on these matters these experiments were undertaken. They follow, in the main, the course adopted in investigating the chloride-containing lead glasses, and will, therefore, be readily understood after reading the reports on this subject. In regard to the opalescence produced in lead glasses solely by the agency of the soluble alkaline sulphate, it appears to us to be rather to be avoided than cultivated; that is to say, whilst the chloride opalescence could find commercial application, we are doubtful of the sulphate. Hence, we have not so far investigated this section of the subject as fully as in the case of the chloride glasses.

I. Preliminary Experiments.

In order to obtain some guidance in larger scale experiments, 26 small scale meltings were carried out. We desired to be able to set the limits, approximately, to the solubility of potassium sulphate, to test very approximately the conditions for the development of opalescence and to ascertain the likely influence of temperature on the melting rate.

In these tests the standard batch employed was as follows :—

Sand	150.
Red lead	100.
Potash	50.
Potassium nitrate	8.
Manganese dioxide	0.5

and to it were added amounts of potassium sulphate in in creasing quantity as stated below.

(1) *Series* 500. *Temperature* 1350°—1400°.

Potassium sulphate added.

500*a*.	*b*.	*c*.	*d*.	*e*.	*f*.	*g*.	*h*.	*i*.	*k*.
0.7	1.4	2.8	5.6	8.4	11.2	14.0	16.8	19.6	22.4

In this series, the temperature was maintained for the first hour of melting at 1350° and raised to 1400° for 2½ hours. The glasses were not stirred.

Under these conditions, whilst 500a, b and c melted readily to clear glasses, excess of potassium sulphate was apparent in 500d and in the subsequent meltings. The presence of excessive sulphate appeared generally to be accompanied by much fine seed, and the slabs of glass after being poured were coated thickly with the salt. During the course of the melting, this salt appeared more freely to rise to the surface the greater the proportion present, so much so that it appeared likely the properties of a glass might be as readily, if not more readily, influenced by batches containing only a moderate amount of sulphate than by one with a big excess.

Subsequent analysis of glasses 500c. and 500f. did show that the amount of sulphate actually dissolved did not depend on using large excess; for in the former, the SO_3 content was found to be higher than in the latter.

(2) *Series* 501. *Temperature* 1300°.

Potassium sulphate.

501*c*.	*d*.	*e*.	*f*.	*g*.	*h*.	*j*.	*k*.
2.8	5.6	8.4	11.2	14.0	16.8	19.6	22.4

The temperature during the first hour was 1275° and for the remaining 2½ hours 1300°. The glasses were stirred.

Glass 500c. showed only a trace of free sulphate on the surface, but all the others of the series had much excess. Although 500c. was clear when a slab of it was poured, slight tendency to opalescence was observed when the slab was maintained at 680—700° for 90 minutes. Slight opalescence was developed under similar conditions in all the subsequent glasses of the series.

One further series of melts was made as follows :—

(3) *Series* 501/2. *Temperature* 1400—1350°.

Batches corresponding to the eight stated in series 501 were again melted. In this case the temperature during the first three-quarters of an hour was maintained at 1400°, being afterwards reduced to 1350° for the remaining 2¾ hours of the melting period. Like Series 501, these were also stirred.

Under these conditions, in which a high initial temperature was employed, neither 501c/2 nor 501d/2 exhibited any residue of salt, but a layer of it showed itself on 501e/2, that is, on the glass made from the batch containing 8.4 parts of K_2SO_4. It was clear that under the conditions described, the maximum amount of potassium sulphate which could be added without leaving a residue was between 6 and 8 parts per 150 parts of sand, or, 4—5.3 per 100.

Experiments on the development of opalescence were also fruitful of interesting results. Whereas in series 500 and 501, opalescence was not well developed under the time and temperature conditions mentioned, 501c/2 when heated in slab form for 2 hours at 700° and then cooled to room temperature in 9 hours, showed a jelly-like opalescence. With 500d/2 the opalescence was still denser.

II. General Procedure in the Large Scale Melting.

The small scale operations had shown quite clearly that even when melting at 1400°, not more than 4 to 5 parts of potassium sulphate per 100 of sand could be used without excess remaining unabsorbed. Larger meltings were now begun either on the 28-lb. or 56-lb. scale, and it will be shown that the actual limit to addition to the batch of potassium sulphate is distinctly smaller than indicated in the small crucible experiments.

The general procedure was very similar to that adopted in the case of the tests with the potassium chloride meltings

being carried out at two different temperatures, one series at 1400°, the other at 1350°. In both cases this initial temperature was maintained only for a period of 5 hours and was subsequently reduced to 1140° and maintained at this level for a further 16 or 17 hours.

Here also, as in the case of the chloride glasses, it seemed desirable to test the extent to which glasses of the same composition could be reproduced. For this reason repeated meltings were made of a number of glasses and the results are set out in Table I. below.

Mention may also be made of the fact that difficulty was found, as with the chloride glasses, in attempting to correlate the composition of the batch with that of the finished glass. This difficulty was associated with the mixing of the dried materials in the batch when it was found that samples taken from different portions of the batch could not be relied on to be sufficiently uniform as to make comparison possible.

As to the batch compositions, these are set out clearly in Table I. The reference to the calculated percentage of SO_3 assumes that all the sulphate has been absorbed by the glass.

TABLE I.

		(a).	(b).	(c).	(d).	(e).
Sand	900	900	—	—	—	—
Red Lead	600	600	—	—	—	—
Potash	300	298	295	290	288	285
Potassium Nitrate ...	48	—	—	—	—	—
Manganese	1	—	—	—	—	—
Potassium Sulphate ...	—	3.1	6.2	12.5	15.5	18.5
Calculated % SO_3 in glass (approx.)	—	0.1	0.15	0.3	0.4	0.5

A. Phenomena Observed during the Melting and Fining Processes.

In Table II. is given a summary of the melting and other phenomena noted in the case of all glasses of Series 502 considered in this report.

TABLE II.

The 502 series (Sulphate free).

	No. 502.	No. 502/2.
Melting.	Free from batch in 2 hours.	Free from batch in 2 hours.
Fining.	Fine in 12 hours.	Almost free from seed in 12 hours—very fine and widely spaced seeds (open boil?) remain to the end.
Waviness.	Wavy at 12 hours—more so at 22 hours.	Very wavy at 12 hours; waviness increased towards end of melting as for No. 502.
Opalescence.	Slight opalescence in the pot.	None.
Colour.	Pink throughout.	Colourless to 4 hours, greenish subsequently and increasing to the end—greener than any of sulphate glasses melted at 1350°.
Working Properties.	Normal except for waviness.	Normal except for waviness.

The 502a series (Sulphate 0.17 per cent.).

	502a.	502a/3.	502a/4.
Melting.	Free from batch in 2 hours.	Free from batch in 2 hours.	Free from batch in 2 hours.
Floating Sulphate.	None.	None.	None.
Fining.	Fine in 10 hours.	Fine in 10 hours.	Some fine seed remained to the end.
Waviness.	Slightly wavy at 6 hours; rather less wavy at the end. Much less wavy than 502.	Slightly wavy at 6 hours, but almost free from wave at the end.	Faintest sign of waviness.
Opalescence.	Very faint at 12 hours and soon disappeared.	None.	None.
Colour.	Pink throughout.	After 1 hour very faint pink. After 5 hours pale green tint. No mixed colours.	As for 502a/3.
Working Properties.	Normal.	Normal or easier than normal.	Normal or easier than normal.

The 502b series (Sulphate 0.37 per cent.).

	502b.	502b/2.	502b/3.
Melting.	Batch free in 2 hours.	Batch free in 2 hours.	Batch free in 2 hours.
Floating Sulphate.	For 2 hours.	For first hour.	For first hour.
Fining.	Almost free from seed in 5 hours—free in 12 hours.	Free from seed in 5 hours.	Almost free from seed in 5 hours—free at 12 hours—seedy boil developed after 18 hours
Waviness.	Very wavy at 3 hours, less so at end, but rather more than 502a.	Very wavy at 3 hours, decreased to end as 502b.	More wavy than 502b,2 throughout, but decreased from start to finish.
Opalescence.	Very slight at 10 hours.	Very slight if any.	None.
Colour.	Pink throughout	At 5 hours colourless; pale green to 16 hours; almost colourless at 18 hours; pale green at end	At 5 hours colourless and then pale green to the end.
Working.	Very slightly easier than 502a.	As 502b.	As 502b.

The 502c series (Sulphate 0.72 per cent.).

	502c.	502c/2.	502c/3.
Melting.	Practically free from batch in 2 hours.	Batch free in 2 hours.	Batch free in 2 hours.
Floating Sulphate.	For 4 hours.	Not after first hour.	Not after first hour
Fining.	A very little fine seed remained throughout—practically plain.	A very little fine seed, as 502c.	As 502c.
Waviness.	Ragged and strong to 3 hours, less wavy towards end—wavier than 502a or 502b, but less so than 502.	Ragged and very wavy during first 3 hours, but less so towards the end.	Not as wavy as 502c/2 in the early stages, but same as 502c/2 at the end.
Opalescence.	Very slight in the pot after 11 hours, obtained in denser form by slow cooling; distinct in the pot after 22 hours.	None in the pot, but by heating and slow cooling could be developed at any stage.	As 502c/2.
Colour.	Pink throughout, slightly decreasing from start to finish.	Greenish tint after 1 hour and increased slightly throughout.	Colourless at 5 hours; greenish at 12 hours; same as 502c/2 at the end.
Working.	As 502b.	As 502b.	As 502b.

The 502d series (Sulphate 0.91 per cent.).

	502d.	502d/2.	502d/3.
Melting.	Batch free in a little over 3 hours.	Batch free in 2 hours.	As 502d.
Floating Sulphate.	For about 12 hours.	For 2 hours.	For 2 hours.
Fining.	Very little seed after 6 hours. Clear in 12 hours.	Plain in 5 hours.	Fine seed present. Very little change from 3 hours to the end.
Waviness.	Ragged and stony to 12 hours. Excluding the salt, the glass was very wavy to 14 hours, but waviness gradually decreased. As wavy as 502.	Not ragged after floating sulphate gone. Very wavy for first 12 hours, but decreased as in 502d.	Not as wavy as 502d/2 in early stages, but same at the end.
Opalescence.	Slight in pot after 9 hours.	None in the pot.	Like 502d/2.
Colour.	Pink throughout, decreasing steadily from start to finish.	4 hours yellowish green. 5 hours pinkish—no green. 12 hours greenish tint. 16 and 18 hours less green. 22 hours greenish to pinkish. Colour very pale.	Greener than 502d/2, green as 502c/3.

The 502e series (Sulphate 1.09 per cent.).

	502e.	502e/2.	502e/3.
Melting.	Batch free in 4 hours, except for floating sulphate.	As 502e.	As 502e.
Floating Sulphate.	For about 12 hours; traces to 16 hours.	For about 12 hours.	For 5 hours.
Fining.	Practically free from seed in 16 hours.	Practically free at 12 hours.	As 502e.
Waviness.	Distinctly wavy, but decreases to the end—waviest of the 502 series.	Wavy as for 502e.	As 502e.
Opalescence.	In pot through-out, decreasing to very slight sign at the end.	Slight in pot to 18 hours.	As 502 /2.
Colour.	Pink throughout, decreasing from start to finish.	6 hours colourless. 12 hours yellowish green tint. 22 hours pale green tint to medium green—mixed as with 502c/3 and 502d/3.	As 502e/2.

Generally speaking, it was found to be considerably easier to duplicate the melting and allied phenomena in the case of the sulphate glasses than with those containing chloride. This fact must be ascribed largely to the substitution of the volatile potassium chloride by this much less volatile potassium sulphate. There were no visible fumes given off from these glasses and the removal of insoluble potassium sulphate occupied a much longer time in general than the removal of chloride. It remained on the surface of the glass as a clear mercurial liquid, in the first stages plainly visible, but later as an invisible film. This floating sulphate influenced the ease of gathering and also apparently the rate of fining. When the floating sulphate was sufficient as to be visible on the surface, gathering was difficult, the sulphate preventing adhesion of the glass to the blowing iron. Further, the sulphate was liable to be trapped in the gathering of glass, either in liquid form, which rapidly solidified to a " stone," or in a " salt blister." The invisible film which was found later in certain meltings did not appreciably affect the gathering of the glass, but the sulphate still caused imperfections in the glass. This suggests a possible difficulty where meltings are made from batches containing sulphate. If the glass were plain whilst a little sulphate remained on the surface the articles made from the glass might be spoiled by inclusions. Our results, however, do not give any indication that this occurs in practice. Whereas in certain of the chloride glasses the metal was free from seed though a little floating chloride remained, the sulphate glasses never became free from seed whilst any sulphate remained on the surface. The presence of the floating sulphate appeared definitely to hinder the removal of seed.

In all except the " e " glasses, the metal was free from batch in two hours. The presence of sulphate appeared to have no effect on the melting rate; it neither hindered nor assisted the melting. Duplicate meltings were in almost every case identical in this respect, but not as regards floating sulphate. The length of time during which this excess of sulphate remained floating was found to be influenced

considerably by very slight variations of temperature, by the amount of batch filled into the pot, and by the geometrical form of the surface of the material in the pot.

Corresponding with the difference in the time of removal of sulphate either by decomposition or absorption there was a difference in the rate of fining, very noticeable in the case of the " d " and " e " glasses. Removal of seed from the sulphate glasses was very difficult, however, particularly in the case of the glasses melted at 1350° and dealt with later in this report.

The degree of waviness in different meltings of the same batch remained practically the same, and the ease with which this duplication was effected may be ascribed to the fact that only slight differences in waviness occurred throughout the series.

Opalescence, which in the case of the sulphate glasses is of quite a different type from that in the chloride glasses, was duplicated almost invariably. The final colour of the glasses was duplicated generally with the exception of the first glass in each section, where it is possible that manganese dioxide was added in excess of the intended quantity.

B. The Ultimate Composition of the Glasses.

The analyses of the glasses which are given in Table III. do not give indication of such satisfactory duplication as was obtained in the case of the chloride glasses. The different meltings of the " a," " c " and " d " glasses show somewhat similar figures, but the " b " and " e " glasses are not in close agreement. Variation in composition does not, therefore, appear to follow the increase of sulphate content of the batch as with the chloride.

TABLE III.

No.	SiO_2	PbO	K_2O	Al_2O_3	Fe_2O_3	MnO	SO_3	Total
502	51.92	35.08	12.70	0.12	0.04	0.07	0.10	100.03
502/2 ...	55.28	31.80	12.82	0.06	0.02	0.06	0.11	100.15
Calc. ...	52.35	34.49	12.97	0.09	0.02	0.05	—	99.97
502a ...	52.40	34.22	12.59	0.18	0.02	0.06	0.24	99.71
502a/3 ...	59.70	28.96	10.82	0.10	0.03	0.04	0.19	99.84
502a/4 ...	59.00	29.85	10.67	0.10	0.02	0.04	0.23	99.91
Calc. ...	52.28	34.43	13.02	0.09	0.02	0.05	0.08	99.97
502b ...	53.72	33.06	12.57	0.18	0.02	0.06	0.32	99.93
502b/2 ...	52.98	33.99	12.61	0.11	0.02	0.05	0.26	100.02
502b/3 ...	53.99	32.90	12.39	0.13	0.03	0.04	0.26	99.74
Calc. ...	52.24	34.40	12.99	0.09	0.02	0.05	0.17	99.96
502c ...	52.59	34.08	12.56	0.26	0.04	0.05	0.28	99.86
502c/2 ...	53.74	33.31	12.74	0.10	0.03	0.05	0.25	100.22
502c/3 ...	53.24	33.93	12.21	0.11	0.01	0.05	0.26	99.81
Calc. ...	52.16	34.35	12.97	0.09	0.02	0.05	0.33	99.97
502d ...	52.86	33.76	12.79	0.08	0.02	0.06	0.21	99.78
502d/2 ...	53.62	32.85	13.07	0.06	0.02	0.05	0.31	99.98
502d/3 ...	53.38	32.47	13.75	0.11	0.03	0.05	0.30	100.09
Calc. ...	52.10	34.32	12.98	0.09	0.02	0.05	0.42	99.98
502e ...	52.84	33.98	12.61	0.02	0.02	0.06	0.29	99.82
502e/2 ...	52.38	33.46	13.37	0.07	0.04	0.06	0.31	99.69
502e/3 ...	53.42	33.09	12.72	0.05	0.02	0.05	0.33	99.68
Calc. ...	52.07	34.29	12.95	0.09	0.02	0.05	0.50	99.97

III. The Amount of Sulphate dissolved in the Potash-Lead Glasses.

Very close agreement is found generally between the amounts of sulphur trioxide in the corresponding glasses. The figures are given in Table IV.

TABLE IV.

Sulphur Trioxide contents of the Glasses.

Glass No.	Temp. of Melting.	Percentage of Sulphur trioxide.	Mean Percentage. 1350°	Mean Percentage. 1400°	Calc. percentage.
502	1400°	0.10	—	0.10	
502/2	1400°	0.11			
502a	1400°	0.24	—	0.22	0.08
502a/3	1400°	0.19			
502a/4	1400°	0.23			
506a/3	1350°	0.14	0.16	—	
506a/4	1350°	0.17			
502b	1400°	0.32	—	0.28	0.17
502b/2	1400°	0.26			
502b/3	1400°	0.26			
506b/2	1350°	0.23	0.22	—	
506b/4	1350°	0.21			
502c/2	1400°	0.25	—	0.26	0.33
502c/3	1400°	0.26			
506c	1350°	0.32	0.30	—	
506c/2	1350°	0.27			
502d	1400°	0.23	—	0.28	0.42
502d/2	1400°	0.31			
502d/3	1400°	0.30			
506d	1350°	0.24	0.27	—	
506d/2	1350°	0.29			
502e	1400°	0.29	—	0.31	0.50
502e/3	1400°	0.33			
506e	1350°	0.32	0.28	—	
506e/2	1350°	0.24			

It will be noted that about 0.1 per cent. of sulphur trioxide is contained in the glass intended to be free from sulphate. This in introduced from the gases in the furnace. The maximum amount of sulphur trioxide capable of being introduced into the English crystal glass under the melting conditions specified at 1350° and 1400° appears to lie between

0.30 and 0.35 per cent. This amount includes that derived from the furnace gases, and assuming this amount to be equivalent to 0.10 per cent. of sulphur trioxide, that introduced from the batch alone is, in these glasses, from 0.20 to 0.25 per cent. In commercial practice, using producer gas, the amount of sulphate introduced from the furnace gases may be different from that in our case where coal gas was used throughout.

If we assume that 0.10 per cent. is the average amount of sulphur trioxide derived from the furnace gases and deduct this from the total amounts actually found in the glasses (see Table V.) it would appear that the "a" and "b" glasses melted at 1400° take up the whole of the sulphate introduced in the batch. With succeeding glasses, the amount of sulphur trioxide remaining in the glass is almost constant, and therefore, as we progress from the "b" to the "e" glasses, increasing amounts of sulphur trioxide are lost. The meltings at 1350° scarcely show the same effect, the amounts of sulphur trioxide introduced into the "a" and "b" glasses melted at that temperature being distinctly lower than those in the corresponding glasses melted at 1400°. Hence it would appear that steadily increasing amounts of sulphur trioxide, introduced in the batch, are lost as one progresses through the series melted at 1350°, and in no case is the whole of the sulphur trioxide introduced in the batch retained in the glass.

TABLE V.

Sulphur Trioxide introduced into the glass from the Potassium Sulphate.

(*a*) Melting at 1400°—series 502.

Glass No.	(A) Mean percentage of SO_3 in the glass, less 0.10 per cent.	(B) Calc. percentage of SO_3.	Difference. B — A.
a	0.12	0.08	−0.04
b	0.18	0.17	−0.01
c	0.16	0.33	0.17
d	0.18	0.42	0.24
e	0.21	0.50	0.29

(*b*) Melting at 1350°—series 506.

Glass No.	(A) Mean percentage of SO_3 in the glass, less 0.10 per cent.	(B) Calc. percentage of SO_3	Difference. B — A
a	0.06	0.08	0.02
b	0.12	0.17	0.05
c	0.32	0.33	0.01
d	0.17	0.42	0.25
e	0.18	0.50	0.32

(*c*) Melting at 1350° with stirring—series 526.

a	0.03	0.08	0.05
b	0.10	0.17	0.07
c	0.20	0.33	0.13
d	0.15	0.42	0.27
e	0.13	0.50	0.37

It will be seen from section (*a*) of Table V. that in the 502 series, assuming 0.10 per cent. of sulphur trioxide to be introduced from furnace gases, there is apparently more sulphur trioxide present in excess than was added as potassium sulphate. Therefore it may be stated that potassium sulphate present to the extent of about 0.3 per cent. of the heavy lead-potash batch or about 2 per cent. of the potash content of such a batch is wholly soluble in the glass melted at 1400°. As the amount of sulphate in the batch increases, the loss of sulphur trioxide from the melting increases. It would appear, however, that melting at 1350° results in a loss of sulphur trioxide no matter how much is present, and stirring further increases the losses. With the unstirred glass the loss of sulphur trioxide varies from 25 per cent., in the glass with least sulphate, to 65 per cent. in that with most added sulphate, the corresponding figures for the stirred glasses being 63 per cent. and 74 per cent. Whereas the glasses melted at 1400° show a marked change as regards removal of SO_3 between " b " and " c," the changes in series 506 and 526 are much more gradual.

The maximum amount of potassium sulphate, therefore, which is retained in the English crystal glass is about 0.76

per cent., equivalent to 0.35 per cent. of sulphur trioxide in the glass. This amount is found in the glass when the amount of potassium sulphate in the batch reaches not more than 0.67 per cent., and where about 0.10 per cent. of sulphur trioxide is introduced from the furnace gases into the glass. When the percentage of potassium sulphate in the batch reaches 0.83 the maximum sulphate content of the glass will be reached irrespective of any sulphur in the furnace gases and some sulphate will also be lost.

IV. A Comparison between the Calculated and Observed Compositions of the Glasses.

In this section, as in section IV. of the report on the chloride meltings, we wish to discuss to what relative extent the various materials are lost from the batch during melting and to what extent the potassium sulphate is decomposed in various circumstances. In Table VI. are given the complete analyses of all the glasses examined. These comprise glasses melted at 1400° and at 1350° without stirring, and at 1350° with stirring.

The calculated compositions of the glasses are derived from the batch compositions, assuming that no loss of material occurs due to any cause except, of course, the normal loss such as carbon dioxide, and also the nitrogen oxides from the nitrate added. The " K_2O " content represents the potassium oxide derived solely from the potassium carbonate and potassium nitrate. The " Total K_2O " content includes in addition the potassium oxide which is assumed to be in combination with the sulphur trioxide in the glass and is, therefore, the total potassium oxide content of the glass as estimated. The " K_2O " content is derived from the latter, therefore, by subtracting an amount of potassium oxide equivalent to that which would be required to combine exactly with the sulphur trioxide present to form potassium sulphate.

TABLE VI.

Chemical Composition of the Glasses.

(*a*) The 502 series melted at 1400°.

Glass No.	SiO_2	PbO	K_2O	Al_2O_3	Fe_2O_3	MnO	K_2SO_4	Total	Total K_2O	SO_3
502	51.92	35.08	12.58	0.12	0.04	0.07	0.22	100.03	12.70	0.10
502/2	55.28	31.80	12.69	0.06	0.02	0.06	0.24	100.15	12.82	0.11
Calc.	52.35	34.49	12.97	0.09	0.02	0.05	0.00	99.97	12.97	0.00
502a	52.40	34.22	12.31	0.18	0.02	0.06	0.52	99.71	12.59	0.24
502a/3	59.70	28.96	10.60	0.10	0.03	0.04	0.41	99.84	10.82	0.19
502a/4	59.00	29.85	10.40	0.10	0.02	0.04	0.50	99.91	10.67	0.23
Calc.	52.28	34.43	12.93	0.09	0.02	0.05	0.17	99.97	13.02	0.08
502b	53.72	33.06	12.19	0.18	0.02	0.06	0.70	99.93	12.57	0.32
502b/2	52.98	33.99	12.31	0.11	0.02	0.05	0.56	100.02	12.61	0.26
502b/3	53.99	32.90	12.09	0.13	0.03	0.04	0.56	99.74	12.39	0.26
Calc.	52.24	34.40	12.79	0.09	0.02	0.05	0.37	99.96	12.99	0.17
502c	52.59	34.08	12.23	0.26	0.04	0.05	0.51	99.76	12.56	0.28
502c/2	53.74	33.31	12.45	0.10	0.03	0.05	0.54	100.22	12.74	0.25
502c/3	53.24	33.93	11.91	0.11	0.01	0.05	0.56	99.81	12.21	0.26
Calc.	52.16	34.35	12.58	0.09	0.02	0.05	0.72	99.97	12.97	0.33
502d	52.86	33.76	12.54	0.08	0.02	0.06	0.46	99.78	12.79	0.21
502d/2	53.62	32.85	12.71	0.06	0.02	0.05	0.67	99.98	13.07	0.31
502d/3	53.38	32.47	13.40	0.11	0.03	0.05	0.65	100.09	13.75	0.30
Calc.	52.10	34.32	12.49	0.09	0.02	0.05	0.91	99.98	12.98	0.42
502e	52.84	33.98	12.27	0.02	0.02	0.06	0.63	99.82	12.61	0.29
502e/2	52.38	33.46	13.01	0.07	0.04	0.06	0.67	99.69	13.37	0.31
502e/3	53.42	33.09	12.33	0.05	0.02	0.05	0.72	99.68	12.72	0.33
Calc.	52.07	34.29	12.36	0.09	0.02	0.05	1.09	99.97	12.95	0.50

(*b*) The 506 series melted at 1350°.

Glass No.	SiO_2	PbO	K_2O	Al_2O_3	Fe_2O_3	MnO	K_2SO_4	Total	Total K_2O	SO_3
507/3	54.51	31.65	13.20	0.38	0.04	0.01	0.22	100.01	13.32	0.10
507/4	54.84	31.50	12.76	0.35	0.07	0.02	0.26	99.80	12.90	0.12
Calc.	52.35	34.49	12.97	0.09	0.02	0.05	0.00	99.97	12.97	0.00
506a	52.74	34.47	11.79	0.08	0.02	0.06	0.63	99.79	12.13	0.29
506a/3	54.08	32.84	12.63	0.11	0.03	0.05	0.30	100.04	12.79	0.14
506a/4	52.86	33.89	12.59	0.09	0.03	0.05	0.37	99.88	12.79	0.17
Calc.	52.28	34.43	12.93	0.09	0.02	0.05	0.17	99.97	13.02	0.08
506b	52.50	33.93	12.60	0.21	0.03	0.05	0.78	100.10	13.02	0.36
506b/2	53.30	33.34	12.45	0.14	0.02	0.05	0.50	99.80	12.72	0.23
506b/4	52.70	33.81	12.54	0.18	0.02	0.05	0.46	99.76	12.79	0.21
Calc.	52.24	34.40	12.79	0.09	0.02	0.05	0.37	99.96	12.99	0.17
506c	52.56	34.88	11.68	0.05	0.03	0.05	0.70	99.95	12.06	0.32
506c/2	52.90	33.73	12.35	0.08	0.02	0.04	0.59	99.71	12.67	0.27
Calc.	52.16	34.35	12.58	0.09	0.02	0.05	0.72	99.97	12.97	0.33
506d	52.46	33.49	13.10	0.17	0.03	0.05	0.52	99.82	13.62	0.24
506d/2	53.52	33.25	12.53	0.10	0.04	0.04	0.63	100.11	12.87	0.29
Calc.	52.10	34.32	12.49	0.09	0.02	0.05	0.91	99.98	12.98	0.42
506e	52.90	33.91	12.08	0.08	0.02	0.06	0.70	99.75	12.46	0.32
506o/2	52.86	33.56	12.84	0.01	0.02	0.05	0.52	99.86	13.12	0.24
Calc.	52.07	34.29	12.36	0.09	0.02	0.05	1.09	99.97	12.95	0.50

(*c*) The 526 series melted at 1350° and stirred.

Glass No.	SiO_2	PbO	K_2O	Al_2O_3	Fe_2O_3	MnO	K_2SO_4	Total	Total K_2O	SO_3
526a	52.72	33.89	12.74	0.06	0.02	0.05	0.28	99.76	12.89	0.13
Calc.	52.28	34.43	12.93	0.09	0.02	0.05	0.17	99.97	13.02	0.08
526b	52.30	34.17	12.79	0.19	0.03	0.05	0.43	99.96	13.02	0.20
Calc.	52.24	34.40	12.79	0.09	0.02	0.05	0.37	99.96	12.99	0.17
526c/2	53.78	32.18	13.15	0.28	0.02	0.06	0.69	100.16	13.52	0.32
526c/3	52.40	33.87	12.98	0.20	0.02	0.06	0.59	100.12	13.30	0.27
Calc.	52.16	34.35	12.58	0.09	0.02	0.05	0.72	99.97	12.97	0.33
526d	52.34	34.01	12.83	0.26	0.04	0.06	0.54	100.08	13.12	0.25
Calc.	52.10	34.32	12.49	0.09	0.02	0.05	0.91	99.98	12.98	0.42
526e	52.78	34.02	12.60	0.16	0.04	0.07	0.50	100.17	12.87	0.23
Calc.	52.07	34.29	12.36	0.09	0.02	0.05	1.09	99.97	12.95	0.50

Dealing with series 502 first, we find that the lead content of the glass made from batch containing no sulphate, is considerably lower than the calculated value, nearly 3 per cent. in fact. The potash content is also lower than the calculated value but only slightly so. Thus the potash is considerably less volatile than the lead in heavy lead-potash batches. This confirms the observations made on glasses 507, which, it may be mentioned, form the starting point of series 506 of the sulphate glasses. The silica content is some 3 per cent. higher than the calculated value owing to the loss of lead oxide.

It is quite obvious that the final glasses of the 502a series differ so much that some big difference must have existed in the batch compositions. Comparison with the calculated composition is, therefore, out of the question.

The silica contents of the " b," " c," " d," and " e " glasses are invariably higher than the calculated values; this was to be expected. The lead oxide contents are invariably lower than the calculated values; again a result to be expected. The potassium oxide content is lower in the glasses " b " and " c " than the calculated amount. In the " d " and " c " glasses it is generally higher, due to loss of sulphur trioxide and lead oxide increasing the apparent potassium oxide content.

The glasses melted at 1350°, series 506, do not show marked differences, and, in fact, agree quite closely with the calculated values for the various constituents. The original glass, Nos. 507/3 and 507/4, made from batch without sulphate, are similar to the glasses 502 and 502/2 in that the lead oxide content is much lower than the calculated value. No marked change as regards further loss of lead oxide occurs with the " a " glass. On the contrary, the addition of sulphate appears to prevent loss of lead oxide. The silica contents of the 506 series are generally lower than those of the 502 series, but still slightly higher than the calculated values. The lead oxide contents are generally

higher than those of the 502 series and only in one case is the apparent loss of lead oxide more than about 1 per cent. The potassium oxide contents vary very little, but show slight excess over the calculated values in the " d " and " e " glasses.

It is thus apparent that in the glasses of the 502 and 506 series the potassium sulphate appears to decompose or to volatilise without noticeable addition of potassium oxide to the glass, until an amount exceeding 0.7 per cent. of potassium sulphate is present in the batch. When this is so, as in the " d " and " e " glasses, it is probable that decomposition of the potassium sulphate results in addition of potassium oxide to the glass in excess of that equivalent to the SO_3 content.

Stirring apparently further stabilises the composition of the glass, the lead oxide contents being nearer the calculated values than in the corresponding glasses of the 506 series, and the potassium oxide contents are, with one exception, higher than the calculated values. Stirring would, therefore, appear to assist in the decomposition of the sulphate, causing presence of less SO_3 in the glass and the addition of more K_2O than in series 502 and 506.

The impurities, alumina and iron oxide, vary very little in amount in series 502 and 506. The alumina contents are frequently below the calculated values, and only in one glass of those two series does the alumina content exceed the calculated value by more than 0.05 per cent. The iron oxide content only in one case exceeds 0.05 per cent. Thus there is no evidence, in these glasses, of increased pot attack due to the presence of sulphate; one would rather conclude that corrosion was reduced.

Stirring had a marked effect apparently on the pot attack since the alumina contents of the glasses of series 526 are very substantially higher than those of series 506 or 502. The iron oxide content, on the contrary, shows a decrease.

V. The Effect of Temperature on the Rate of Melting and on other Properties of Molten Potash-Lead Glasses.

In Table II. there has already been given a summary of the behaviour of the glasses of the 502 series. Table VII. gives a similar summary of the 506 series, including the glasses 507 melted at 1350° without the addition of sulphate.

(*a*) *Melting.*

At 1350° the introduction of increasing amounts of potassium sulphate retarded the rate of melting. There was a difference of four hours, approximately, between the time required for the disappearance of batch in the " a " glasses and the " e " glasses. This, of course, only applies when any floating sulphate is neglected. Traces of sulphate were found on the surface of the " a " glasses up to five or six hours from the time of the second filling, and on one of the " e " glasses sulphate floated for 16 hours before finally disappearing. It floated, like water, on the surface of the " c," " d," and " e " glasses. It did not volatilise in the heavy fume form as with the chloride, but was removed much more slowly. As the amount of sulphate added in the batch increased, the longer it remained on the surface, the longer was the batch in completely melting, and, as already indicated, the less was the amount of lead oxide and potassium oxide lost by volatilisation.

An increase in the temperature to 1400° resulted in an increased melting rate and a reduction in the difference in rate between the various glasses; since the " a " glasses of both series 506 and 502 melted in approximately the same time. As the amount of floating sulphate was only slightly reduced, however, and also the time it remained floating on the surface, it follows that the increase of temperature had no substantial effect on the melting rate so far as obtaining a pot of glass ready for working without skimming.

(*b*) *Fining (freedom from seed).*

Only the " d " and " e " glasses of series 506 became free from seed. The presence of sulphate in the batch exerted a very adverse influence on fining. A fine seed was retained persistently. The retention of seed did not increase with increasing sulphate in the batch; the " b " glasses were the worst and the " a " glasses little or no better. In none of the glasses of this series was there a case of recurrence of seed. The sulphate did not appear to assist in fining in any way and increasing quantities of sulphate in the batch had no progressive influence.

Temperature had a marked influence on the fining rate of the sulphate glasses. Series 502 fined generally at a much quicker rate than series 506. The " a," " b " and " d " glasses fined more quickly than the original glasses without sulphate. Even though the above glasses were obtained free from seed, duplicate meltings contained fine seed. The "b " glass fined most readily; there was no regular increase or decrease in fining, but the " e " glass was the longest in fining. There was no doubt that a 50° rise in temperature, from 1350° to 1400°, was much more effective in improving the rate of fining than any possible effect of the sulphate detrimental or otherwise. The actual effect of the sulphate at 1400° was to retard fining, but not seriously.

(*c*) *Waviness.*

As with melting, waviness showed no regular progression with increasing sulphate content. The glasses " a " and " b " were distinctly wavy but less so than the glasses 507. The " c " glass was the waviest of the series, and the " d " and " e " glasses were only a very little less wavy. In all cases there was an increase of waviness from start to finish as with the chloride glasses. The increase, however, was quite small after about 6 hours except in the case of the " c " glass. The " c " glass showed signs of abnormality in other ways, and it would appear as though the amount

of sulphate added to the " c " batch is sufficient to provide the maximum quantity of sulphate soluble in the glass and to exert a maximum influence on the properties of the glass. The " d " and " e " glasses have their properties modified probably by the presence of a considerable amount of excess sulphate. When floating sulphate was present and glass could be gathered it was very ragged. In general, the sulphate glasses were more wavy than the chloride glasses at the same temperature.

The 502 series, melted at 1400°, showed distinctly different phenomena as regards waviness. The increased melting temperature considerably checked the waviness. The " a " glasses were almost free from waviness, and it would appear that the addition of a little sulphate when melting at 1400° would be beneficial in lead crystal glasses as regards reduction of the tendency to waviness. Although the " b " glasses were very wavy in the early stages, they were very little more wavy at the end than the " a " glasses. The " c " glasses were more wavy than the " a " and " b " glasses, and all three were less wavy than the original glasses 502. The " d " and " e " glasses were more wavy than glasses 502, the " e " being more wavy than the " d " glass. In melting at 1400°, there is, therefore, a regular progressional increase in waviness, as the proportion of sulphate in the batch increases. It is also noteworthy that at 1400° the waviness in the sulphate glasses decreases from start to finish of the melting and does not increase as with the chloride glasses and the sulphate series 506 melted at 1350°.

To summarise, the benefit of high temperature in melting crystal glasses of this type is once more made apparent, particularly where the potash or other materials contain potassium sulphate as an impurity. The presence of this sulphate in the batch causes a decrease in the rate of melting and has a very adverse effect on the rate of fining. Small amounts of sulphate decrease the tendency to waviness in the potash lead glass.

TABLE VII.

The 507 Series (No sulphate in batch).

	No. 507.	No. 507/2.	No. 507/3.	No. 507/4.
Melting	Batch free after 2 hrs. Very little remained after 1 hour.	As 507.	As 507.	As 507.
Fining	Free from seed in 17 hours.	A little small seed after 22 hours.	As 507/2	As 507/2
Waviness ...	Waviness showed after 2 hours and thereafter altered very slightly if at all.	As 507.	As 507.	As 507
Opalescence..	None.	None.	None.	None.
Colour	Pink to 17 hrs. Faintly yellowish green at end.	Pink to 12 hrs. Faintly yellowish pink to 17 hours. Colourless.	Pink to 12 hours. Colourless.	Yellowish or colourless to 12 hours. Greenish to 17 hours. Very pale green at the end.
Brightness...	Normal. No really sub	Normal. stantial diffe	Normal. rence betwee	Normal. n any of them
Working ...	Normal thro	ughout. Wa increase in	viness causes viscosity.	apparent

The 506a series (Sulphate 0.17 per cent.).

	506a.	506a/2.	506a/3.
Melting ...	Clear of batch in 3 hours.	Practically free from batch in 2 hours. None after 3 hours.	As 506a/2.
Floating Sulphate	Only in specks on the surface up to 6 hours.	Traces up to 3 hours.	As 506a/2.
Fining ...	A little fine seed at 17 hours. Almost free from seed in 22 hours.	A little fine seed remained at the end—little change during last 18 hours.	As 506a/2.
Waviness ...	Distinctly wavy up to 6 hours, only slightly more wavy at end.	Distinct increase in waviness at 12 hours, but only a slight increase from that to the end.	As 506a/2.
Opalescence	Very faintly opalescent if at all.	No sign of opalescence.	As 506a/2.
Colour ...	Better colour than original glass 507, but variable—pink	Pink tint 1 hour. More at 5 hours. Pale green 12 hours, greener 17 hours. Final glass mainly colourless, but parts pink and green.	Pink tint to 2 hours. Colourless at 3 hours, to pale green at 12 hours. A little darker at end.
Working ...	Normal or	slightly improved glass without sulph	on that of the ate.

The 506b series (Sulphate 0.37 per cent.).

	506b.	506b/2.	506b/4.
Melting ...	Free from batch in 3 hours.	Clear in 3 hours.	Clear in 3 hours.
Floating Sulphate	In stony form to 3 hours.	A little up to 3 hours.	As 506b/2.
Fining ...	Fine seed (more than in a/2 at 16 hours). No change to the end.	As 506b.	A little less seed than 506b/2.
Waviness ...	Very slightly less wavy than a/2.	Distinctly wavy throughout—slight increase from start to finish, but rather less than a/2 and more than 506b.	As 506b/2.
Opalescence	Very slight, if any.	None.	None.
Colour ...	Pink throughout.	Pink to 5 hours. Colourless at 12 hours. Pink to green from bottom to the top finally.	Very pale green at 5 hours. Pink to pale green bottom to top at end.
Working ...	Better	than normal in	each case.

The 506c series (Sulphate 0.72 per cent.).

	506c.	506c/2.
Melting ...	Clear in 4 hours, except a trace of salt on the surface.	Clear of batch in 4 hours.
Floating Sulphate	Fairly extensive to 3 hours. Trace at 4 hours. None at 5 hours.	Very much up to 3 hours. None at 4 hours.
Fining ...	Seed very fine at 10 hours and remained same to the end.	Practically free from seed in 8 hours, but a little remained, very fine, at the end.
Waviness ...	Slight wave at 6 hours, which increased very considerably towards the end—waviest of the 506 series.	As for 506c.
Opalescence	Slight throughout—decrease from start to finish.	None in glass in pot, but slight on reheating in thick pieces.
Colour ...	Pink throughout.	Pinkish to 5 hours—pale green to 16 hours—pale green at the end on the surface, to pale pink at bottom of pot. Greatest range of colour at end of any 506.
Working ...	As for	" b " series.

The 506d series (Sulphate 0.91 per cent.).

	506d.	506d/2.
Melting ...	Apparently free from batch in 4 hours.	As 506d.
Floating Sulphate	On surface for 6 hours.	None after 5½ hours.
Fining ...	Very little seed at 16 hours. Free from seed at the end.	Still a little fine seed at the end.
Waviness ...	As 506d/2.	Distinct at 6 hours—a little more wavy at the end.
Opalescence	Quite milky to 4 hours; afterwards slightly less to the end.	On slow cooling following reheating.
Colour ...	Pink throughout.	Pink at 4 hours. Yellowish pink at 6 hours. Colourless tending to greenish at 12 hours. Pinkish at 16 hours—mixed colours at the end.
Working ...	As for " b "	throughout.

The 506e series (Sulphate 1.09 per cent.).

	506e.	506e/2.
Melting ...	Clear of batch in 6 hours.	Clear of batch in 5 hours.
Floating Sulphate	Up to 13 hours and traces up to 16 hours.	Up to 12 hours.
Fining ...	Almost free from seed at 10 hours. Free from seed at 16 hours.	Fine seed at 16 hours, and a very little remaining at the end.
Waviness ...	Very ragged up to 13 hours. Quite wavy at the end, but no more than "b," "c," or "d."	As 506e.
Opalescence	Distinctly opalescent throughout—glass surface rather dim.	Not so opalescent as 506e, but appears on slow cooling.
Colour ...	Pink throughout.	Colourless at 4 hours. Colourless to greenish at end.
Working ...	As for	"b" series.

VI. The Effect of Intermittent Mechanical Stirring.

A. The Effect on the Melting Rate and General Properties.

The glasses on which the effect of stirring was tried corresponded in batch composition with the glasses in series 506. They were melted under the same temperature conditions and were stirred at intervals as indicated in Table VIII.

TABLE VIII.

Stirring Times in Series 526.

No. of Glass.	Times (hours after second filling).
526a	1, 3 and 5.
526b	1, 3, 5 and 16.
526c/2	1, 3 and 5.
526c/3	1, 3, 5 and 12.
526d	1, 3 and 5.
526e	1, 3, 5 and 16.

Stirring (see Table IX.) did not cause a great difference in the melting rate as compared with the 506 series, but it was certainly improved. Floating sulphate was very materially reduced, particularly in the " d " and " e " glasses.

No improvement was brought about in fining rate, however, all the glasses remaining more or less seedy. There is no doubt whatever about the effect of sulphate in the production of seediness, particularly when the glasses are melted at 1350°.

Waviness was most changed and the " a " glass, which was stirred at 1, 3 and 5 hours, was as wavy as any sulphate glass made. The " b " glass, stirred in addition after 16 hours, was less wavy at the end than the " a " glass, but more wavy than the unstirred " b " glass. Glasses " c/2 " and " c/3 " were both less wavy than the " b " glass, and, in fact, less so than any other stirred glass. On the contrary, the 506c glasses were the most wavy of the 506 series, being a little more wavy than the " d " and " e " glasses. The 526e/3 glass was stirred at 12 hours besides at the three earlier stages. It was no less wavy in consequence. The later stirring did not appear to have so pronounced an effect on the sulphate glasses as on the chloride glasses. The " d " glass was not very materially improved by stirring, but the " e " glass was certainly better than the 506e glasses as regards waviness and was no more wavy than 526c/2 or 526c/3. It is possible that a slight improvement might have been made in the " d " glass if it had been stirred after 16 hours.

Generally speaking, stirring slightly improved the rate of melting and distinctly increased the rate of removal of excess sulphate. It had no appreciable effect on fining as regards removal of seed, but increased considerably the waviness of the glasses with least sulphate ("a " and " b ") and only slightly improved the later glasses.

TABLE IX.

Properties of Series 526.

No. of glass.	526a.	526b.	526c/2.	526c/3.	526d.	526e.
Melting ...	Batch free in less than 2 hours.	As 526a.	Batch free in less than 3 hours.	As 526c/2.	Batch free in 4 hours.	Batch free in 5 hours.
Floating Sulphate	None.	None.	For $3\frac{1}{2}$ hours.	For 3 hours.	For 4 hours.	For 6 hours.
Fining ...	Fine seed throughout — no change after 12 hours.	As 526a.	As 526a, perhaps a little less seed.	As 526a.	As 526a.	A little seed, but better than any others of series 526.
Waviness ...	Slight in early stages, but increased until as marked as any at the end.	As 526a in early stages, but less at the end.	As 526a in early stages, but less than 526b at the end.	As 526c/2.	As 526a.	As 526c/2.
Opalescence	None.	None.	As 506c/2.	As 506c/2.	As 506d/2.	As 506e/2.
Colour ...	Pink to 6 hours. Colourless to greenish to 16 hours. Variable at end.	Pink to 16 hours. Variable at the end.	As 526b.	As 526b, but less green.	Greenest sulphate glass.	Colourless at 16 hours. Variable at the end.

B. The Effect on the Ultimate Composition of the Glasses.

The silica contents (see Table VIc.) are generally lower than those of either series 502 or 506. On the contrary, the lead contents are rather higher and also the potassium oxide contents. Stirring, therefore, appears relatively to assist in the volatilisation of silica, although the silica contents are generally higher than the theoretical. The lead oxide contents are in all cases below the theoretical amount and this probably accounts largely for the higher percentage of silica.

The potassium oxide content, that is, the potassium oxide presumably derived from the potassium carbonate and potassium nitrate, tends to be greater than the calculated amount the greater the amount of potassium oxide introduced as potassium sulphate. In Table X. are given average values for the potassium oxide contents of all glasses after deducting the corresponding calculated amounts.

TABLE X.

Average Values for Potassium Oxide contents of all the Glasses after deducting the corresponding calculated amounts.

	Excess of found K_2O over calc. K_2O.			Excess of found K_2O as K_2SO_4 over calc. K_2O as K_2SO_4			Excess of total K_2O over total K_2O as calculated.		
Glass.	Series 502.	Series 506.	Series 526.	Series 502.	Series 506.	Series 526.	Series 502.	Series 506.	Series 526.
a	−1.83	−0.59	−0.19	+0.16	+0.14	+0.06	−1.66	−0.45	−0.13
b	−0.63	−0.26	0.00	+0.16	+0.11	+0.03	−0.47	−0.15	+0.03
c	−0.35	−0.56	+0.49	−0.12	−0.04	−0.04	−0.47	−0.60	+0.45
d	+0.39	+0.33	+0.34	−0.17	−0.06	−0.20	+0.22	+0.27	+0.14
e	+0.18	+0.11	+0.24	−0.23	−0.27	−0.32	−0.05	−0.16	−0.08

In series 502, the potassium oxide, presumably derived from the potassium carbonate and potassium nitrate, after showing a distinct deficit compared with the calculated amount in the "a" glass, increases to a surplus in the

" d " glass. A similar increase is shown by the series 506, but the extremes, the " a " and " d " glasses, do not show such high values. Stirring still further reduces this deficit in the " a " and " b " glasses, and shows a maximum surplus in the " c " glasses. Stirring quite evidently reduces the volatilisation of the potassium oxide derived from the carbonate and nitrate.

The potassium oxide content presumably derived from the potassium sulphate shows in all cases the reverse of the above phenomena. Whilst the potassium oxide so obtained in all the " a " and " b " glasses appears in excess of the calculated amount, in the " c," " d " and " e " glasses there is an apparent increasing loss of potassium oxide as the amount of potassium sulphate in the batch increases.

In the " a " and " b " glasses, lowering of temperature, and stirring, still further lower the surplus of potassium oxide over the calculated. In the " c " glasses the same phenomena are exhibited as regards the deficit. With the " d " and " e " glasses, however, the reverse applies to the deficits which increase with lowering of temperature and still more so with stirring. These differences appear to be due to the relative amounts of decomposition and volatilisation of the sulphate occurring in the different series. In the first three glasses, " a," " b " and " c," removal of potassium oxide (introduced as sulphate) is hindered by lowering the temperature and still further by stirring, whilst in the " d " and " e " glasses it is increased.

From a big deficit in total potassium oxide content in the 502 series, there is a steady increase to a surplus in the " d " glass. In the series 506, however, there is an increased deficit from " a " to " c " and the relative increase to a surplus in the " e " glass. Stirring causes a reduced deficit in the " a " glass, produces a surplus in the " b " and " c " glasses, but from there a decrease in surplus in the " d " glass to a slight deficit in the " e " glass.

The general effect of stirring is, therefore, to reduce the total volatilisation of potassium oxide up to the " c " glass,

but in the " d " and " e " glasses it tends rather to increase the loss as compared with series 502, but less so as compared with series 506. It causes also an apparent loss of silica as compared with corresponding glasses of series 502 and 506. The sulphur trioxide content of the glasses does not appear to vary with the alumina; but, on the other hand, if one can judge by the alumina content of the glasses, the attack upon the pot is very greatly increased by stirring.

VII. The Production of Opalescence by dissolved Sulphate in Potash Lead Glasses.

In the paper by Cauwood and Turner, already quoted in Part I. of this report, it was stated that an amount of 0.25 per cent. of sulphate (SO_3) in a crystal glass was sufficient for the production of opalescence. This was confirmed by our early experiments and no modification of that view is necessary as the result of more extensive tests.

The production of opalescence by sulphate does not call for the lengthy treatment devoted to that produced by the chloride since the opalescence is not so fugitive or liable to change due to the volatile nature of the compound causing the opalescence. Variation of the melting temperature from 1350° to 1400° does not appear to exert any great influence on the production of opalescence, but stirring is distinctly effective. The opalescence might occur, as with the chloride glasses, (*a*) during the melting process and standing in the pot, or (*b*) as the result of reheating or of slow cooling of the glass.

As regards opalescence in the pot, some little comment is necessary. In any case, the opalescence was exceptionally slight. It appeared, as already indicated in Part I., after 12 hours from the outset in the case of 502 and 502a; 10 hours with 502b and 11 hours with 502c; 9 hours with 502d and with 502e at an early stage. It disappeared rapidly, however, and only one of the above glasses was opalescent at the end of the melting, this being 502c. Corresponding members of the series 506 showed similar

phenomena, the opalescence being rather denser, appearing earlier and being later in disappearing. In no case was a glass of series 526 opalescent in the pot.

Table XI. gives a summary of the conditions under which opalescence appeared in the pot. The duration of the opalescence appeared to bear no relation to the amount of sulphate in the finished glass, but it increased with the amount of sulphate introduced in the batch. Rise of temperature undoubtedly reduced the tendency to opalescence which, as mentioned previously, was in all cases very faint indeed. Only in 506e was the opalescence apparent at the end of the melting, and this glass contained more sulphate than any of the 506 glasses quoted. The opalescence did not appear in all glasses, and in most of those melted subsequent to the preparation of Part I. of this Report no opalescence whatever appeared in the pot. It is possible, therefore, that the improved method of batch mixing employed in preparing the later glasses, now here described, reduced the tendency to opalescence in the pot, in fact, almost eliminated it. Stirring certainly removed the tendency to produce opalescence in the pot.

TABLE XI.

Production of Opalescence during Melting and Standing.

Glass.	Percentage of K_2SO_4 in the batch.	Stage at which opalescence is apparent.	Duration of opalescence.	SO_3 in finished glass.
502	—	After 12 hours very slight	2 hours	0.10
502a	0.17	Ditto	2 ,,	0.24
502b	0.37	After 10 hours very slight	2 ,,	0.32
502c	0.72	After 11 hours very slight	3 ,,	—
502d	0.91	After 9 hours very slight	5 ,,	0.21
502e	1.09	After 4 hours very slight	7 ,,	0.29
507	—	None	—	—
506a	0.17	After 3 hours slight	8 hours	0.29
506b	0.37	Ditto	8 ,,	—
506c	0.72	Ditto	19 ,,	—
506d	0.91	Ditto	19 ,,	0.24
506e	1.09	After 2 hours slight	20 ,,	0.32

The Production of Opalescence by Reheating.

The observations in connection with the production of opalescence by reheating the sulphate-containing glasses were made (1) on the glass as it was worked from the furnace and made into rod, and tubing, (2) on bulbs specially blown for the test, and (3) on pots of glass treated as described below.

As distinct from the chloride glasses, which could be obtained perfectly clear and the opalescence produced very quickly during reheating, the sulphate glasses are very uncertain. The opalescence in the sulphate glasses does not appear during reheating, that is, whilst the temperature of the glass is rising. It appears during cooling and only where the rate of cooling is sufficiently slow. In many cases where the reheating of bulbs, of the same thickness as previously used when testing the chloride glasses, produced no sign of opalesence, thicker ones, which therefore cooled down more slowly, showed some opalescence. Again, when a bulb occasionally failed to develop opalescence, the thicker part of the glass, close to the pipe nose, which cooled more slowly, showed signs of opalescence.

Opalescence did not occur in any of the finished " a " and " b " glasses and has not been produced in them by any reheating method so far tried by us. The opalescence first appeared with the " c " glasses and was as dense as that obtained with the " d " and " e " glasses. If opalescence could be developed in a glass by reheating and cooling it was of the same type and intensity whether the glass was " c," " d " or " e ". It would, therefore, appear that either the sulphate contents of the glasses are very similar or the intensity of the opalescence does not depend entirely on the amount of sulphate present in the glass. The sulphate contents of the glasses were not so widely different as the chloride contents in the chloride glasses, but there is distinct variation. In those glasses in which opalescence could be produced, the potassium sulphate content ranged from 0.46 to 0.72 per cent., or, in terms of sulphur trioxide, 0.21 to 0.33

per cent. This variation did not cause any change in the intensity of the opalescence.

The opalescence produced in the glasses by sulphate is not of the same type as that produced by chloride. It is not so dense or so white, but is of a bluish, smoky type, with the appearance of a well-stirred, gelatinous, aluminium hydroxide precipitate. The normal annealing process or cooling to room temperature from 700°-800° in 5 hours both tend to produce opalescence, but quick chilling prevents opalescence in all cases.

Whereas reheating the chloride glasses to 450° or 500°, holding at that temperature for two hours, and then cooling slowly, produced opalescence in a glass previously cooled to ordinary temperatures, reheating of certain " c " and " d " sulphate glasses was ineffective. This was true even when the heating was carried up to 900° with various rates of heating and cooling.

Glass transferred to pots and maintained at 900° and 700°, as described in the tests on the chloride glasses, gave opalescence in the " c," " d " and " e " types, but not in the " a " or " b " glasses. The opalescence so obtained was not more dense than that obtained by reheating and cooling during working. No difference was traceable between the " c," " d " and " e " glasses as regards the density of the opalescence, which was of the type already described.

VIII. The Influence of Sulphate Concentration on the Production of Opalescence.

In Table XII. all the data are given concerning the development of opalescence in the glasses.

TABLE XII.

Glass	Temp. of Melting	Treatment during Melting	Per cent. of SO_3 in finished Glass	Calc. per cent. of SO_3	Opalesence.
502a	1400°	Normal ...	0.24	0.08	After 12 hours in pot (2); none by reheating.
502a/3	1400°	,, ...	0.19	0.08	None.
502a/4	1400°	,, ...	0.23	0.08	None.
506a	1350°	,, ...	0.29	0.08	After 3 hours in pot (8); none by reheating.
506a/3	1350°	,, ...	0.14	0.08	None.
506a/4	1350°	,, ...	0.17	0.08	None.
526a	1350°	Stirred ...	0.13	0.08	None.
502b	1400°	Normal ...	0.32	0.17	After 10 hours in pot (2); none by reheating.
502b/2	1400°	,, ...	0.26	0.17	None.
502b/3	1400°	,, ...	0.26	0.17	None.
506b	1350°	,, ...	0.36	0.17	After 3 hours in pot (8); none by reheating.
506b/2	1350°	,, ...	0.23	0.17	None.
506b/4	1350°	,, ...	0.21	0.17	None.
526b	1350°	Stirred ...	0.20	0.17	None.
502c	1400°	Normal ...	0.28	0.33	After 11 hours in pot (11); also by reheating.
502c/2	1400°	,, ...	0.25	0.33	None in pot; but by reheating.
502c/3	1400°	,, ...	0.26	0.33	None in pot; but by reheating.
506c	1350°	,, ...	0.32	0.33	After 3 hours in pot (19); also on reheating.
506c/2	1350°	,, ...	0.27	0.33	None in pot; slight on reheating.
526c/2	1350°	Stirred ...	0.32	0.33	None in pot; slight on reheating.
526c/3	1350°	,, ...	0.27	0.33	None in pot; slight on reheating.
502d	1400°	Normal ...	0.21	0.42	After 9 hours in pot (5); also by reheating.
502d/2	1400°	,, ...	0.31	0.42	None in pot; but by reheating.
502d/3	1400°	,, ...	0.30	0.42	None in pot; but by reheating.
506d	1350°	,, ...	0.24	0.42	After 3 hours in pot (19); also by reheating.

TABLE XII. (continued).

Glass	Temp. of Melting	Treatment during Melting	Per cent. of SO_3 in finished Glass	Calc. per cent. of SO_3	Opalescence
506d/2	1350°	,, ...	0.29	0.42	None in pot; but by reheating.
526d	1350°	Stirred ...	0.25	0.42	None in pot; but by reheating.
502e	1400°	Normal ...	0.29	0.50	After 2 hours in pot (7); also on reheating.
502e/2	1400°	,, ...	0.31	0.50	After 2 hours in pot (17); also on reheating.
502e/3	1400°	,, ...	0.33	0.50	After 2 hours in pot (17); also on reheating.
506e	1350°	,, ...	0.32	0.50	After 2 hours in pot (20); also on reheating.
506e/2	1350°	,, ...	0.24	0.50	Only very slight in pot (18); also on reheating.
526e	1350°	Stirred ...	0.23	0.50	None in pot; but on reheating.

The figures in brackets in the last column indicate the duration in hours of the opalescence in the pot.

Examination of the table shows that glasses containing 0.20 per cent. of sulphur trioxide or less do not give opalescence either during the melting process or by reheating the finished glass. One glass, 502d, has less than 0.24 per cent. of sulphur trioxide and still gives opalescence both in the pot and on reheating. Such behaviour is exceptional. Generally speaking, it would appear that about 0.24 per cent. of sulphur trioxide must be present in the glass before the tendency to opalescence becomes noticeable. The conditions of melting appear to have some slight influence on the phenomenon.

In regard to the appearance of opalescence in the pot itself, it was found, under the conditions of these experiments, that careful batch mixing prevented it almost completely. Stirring the glass had a similar effect.

Melting at 1400° instead of at 1350° appears to reduce the duration of the opalescence in the pot; only one glass,

502c, melted at 1400°C, was opalescent in the pot at the end of the melting, whilst three glasses melted at 1350° remained opalescent in the pot to the end.

Contrary to what appears to be the case with the tests on chlorides, the glasses melted at the higher temperature did not require a higher percentage of sulphate for the production of opalescence. Certain glasses containing 0.24 per cent. of sulphur trioxide or more only developed opalescence in the pot, but not on reheating. None of these glasses remained opalescent in the pot to the end of the melting or even beyond 14 hours. Only two finished glasses with more than 0.24 per cent. of sulphur trioxide did not develop opalescence at some period during their production. These glasses are noted in Table XIII.

TABLE XIII.

Glass.	Temp. of Melting.	Treatment during melting.	SO_3 Content.	Opalescence.
502a	1400°	Normal	0.24	In pot only.
502b	1400°	,,	0.32	,, ,, ,,
506a	1350°	,,	0.29	,, ,, ,,
506b	1350°	,,	0.36	,, ,, ,,
502b/2	1400°	,,	0.26	None.
502b/3	1400°	,,	0.26	None.

It will be noticed that they are all "a" or "b" glasses and that the two giving no opalescence at all belong to the later batch of glasses melted and accordingly were made from batches which were better mixed. On examining the composition (see Table XIV.) of these glasses with a view to finding whether that had any possible influence on the lack of opalescence, we find that the potash content is below the average potash content (12.5 per cent.) of the glasses which give opalescence, and the alumina generally considerably above the average, namely, 0.07 per cent.

TABLE XIV.

Glass No.	SiO_2	PbO	K_2O	Al_2O_3	Fe_2O_3	MnO	K_2SO_4	Total	Total K_2O	SO_3
502a	52.40	34.22	12.31	0.18	0.02	0.06	0.52	99.71	12.59	0.24
502b	53.72	33.06	12.19	0.18	0.02	0.06	0.70	99.93	12.57	0.32
506a	52.74	34.47	11.79	0.08	0.02	0.06	0.63	99.79	12.13	0.29
506b	52.50	33.93	12.60	0.21	0.03	0.05	0.78	100.10	13.02	0.36
502b/2	52.98	33.99	12.31	0.11	0.02	0.05	0.56	100.02	12.61	0.26
502b/3	53.99	32.90	12.09	0.13	0.03	0.04	0.56	99.74	12.39	0.26

The silica and lead oxide contents vary above and below the average. Evidently there is little to be gained by pursuing this line, although there does seem to be a tendency for the glasses, which do not give opalescence, to be harder than those which do so.

If opalescence in the potash lead crystal glasses is to be avoided the sulphate content of the glass must not be more than 0.24 per cent. of sulphur trioxide or 0.52 per cent. of potassium sulphate. Where the sulphate content of the glass rises above 0.20 per cent. of sulphur trioxide or 0.43 per cent. of potassium sulphate, opalescence is possible but not at all probable. Owing to the possibility of absorption of sulphur dioxide from the furnace gases, the amount of sulphur trioxide which may be introduced safely in the form of sulphate in the batch may considerably be reduced. The reduction will depend, of course, upon the percentage of sulphur dioxide in the gases and their accessibility to the glass.

If we assume the average 0.10 per cent. of sulphur trioxide introduced in our glasses to be a general average, then the safety figures for the sulphur trioxide introduced from the batch will be 0.10 per cent. of sulphur trioxide or 0.22 per cent. of potassium sulphate. These figures, with good batch mixing and higher melting temperature, may be extended to 0.14 per cent. of sulphur trioxide or 0.30 per cent. of potassium sulphate without danger of opalescence either in the pot during melting or on reheating.

The figures mentioned are presented in another form in Table XV., where also the corresponding percentage of sulphate permissible in the potassium carbonate is indicated when the ordinary crystal batch is used.

TABLE XV.

Limit of Impurity.	For complete absence of Opalescence.	For absence of Opalescence with thorough batch mixing and high founding temperature.
A. Percentage of SO_3 in glass ...	0.20	0.24
B. Percentage of K_2SO_4 in glass	0.43	0.52
C. Percentage of SO_3 in glass permissible from batch alone	0.10	0.14
D. Ditto K_2SO_4	0.22	0.30
Corresponding percentage permissible in K_2CO_3.		
A.	1.15	1.37
B.	2.45	2.97
C.	0.58	0.80
D.	1.23	1.71

Summary and General Conclusions.

1. Twenty-six small experimental meltings and nearly forty larger meltings (28-lbs. and 56-lbs.) of English crystal glass batches containing potassium sulphate in varying amount have been made. One series of meltings was carried out at 1400°, another series at 1350°.

2. With dried batch materials it was not found possible to obtain perfectly homogeneous batch, so that comparison of the batch composition with the ultimate glass composition could not be made.

3. Repeated meltings of a number of the glasses showed that so far as the general phenomena observed during the melting process are concerned, reproduction of any particular type of glass was a comparatively easy matter, the results in the different meltings being almost identical.

4. The batches contained amounts of potassium sulphate varying from 0.35 to 2.06 parts per 100 of sand. With 0.35 and 0.7 parts in the batch no undecomposed sulphate was found on the surface of the glass at any stage, but when the amount exceeded 0.7 a more or less thick layer of excess sulphate was obtained and persisted for a period determined mainly by the amount of the excess.

5. With a distinctly visible layer of floating sulphate gathering of the glass was difficult, the sulphate layer preventing adhesion to the blowing iron. A thin film, however, did not cause difficulty in gathering.

6. Whether the sulphate layer was distinctly visible or invisible, gatherings of glass made when it was present contained potassium sulphate which rapidly formed either a stone or a salt blister.

7. The presence of floating sulphate appeared quite definitely to hinder the removal of seed from the glass. This was particularly the case when the glasses were melted at the lower temperature of 1350°.

8. The length of time during which excess of sulphate remained floating on the surface was found to be influenced by slight variations of temperature, by the amount of batch filled into the pot, and by the geometrical form of the surface of the material in the pot.

9. The maximum amount of sulphate found dissolved in the glasses was, in terms of SO_3, in the neighbourhood of 0.3 per cent. At 1350° the range of values was 0.16 to 0.30 per cent. SO_3. At a temperature of 1400° the corresponding values were 0.22 to 0.31 per cent. SO_3. The glass to which no sulphate was added contained 0.1 per cent. of SO_3 derived from the furnace gases. If the maximum amount of SO_3 dissolved be agreed on as 0.35 per cent., this is equivalent to 0.76 per cent. of potassium sulphate in the glass.

10. The analytical composition of the finished glasses was compared with the values from the batch composition.

From such comparison, it appeared that the presence of sulphate, generally speaking, hindered the volatilisation of lead oxide.

11. An increase of the melting temperature from 1350° to 1400° resulted in a very marked increase in the melting rate and the glass became plain much quicker at the higher temperature.

12. Small amounts of sulphate not exceeding 0.6 per cent. appeared to diminish the tendency to waviness in lead glasses.

13. Intermittent stirring of the glass during melting was found to improve slightly the rate of melting and to increase the rate of removal of the excessive sulphate. It did not appear to have any appreciable effect on the rate of fining.

14. The presence of sulphate in the batch occasionally produced slight opalescence even in the melting pot. Generally speaking, however, its occurrence was unusual. The tendency to opalescence increased with increasing amount of sulphate in the batch. In any case, thorough batch mixing either hinders or even inhibits the opalescence from appearing during the melting process.

15. Opalescence in lead glasses is only produced when an amount of sulphate equivalent to not less than 0.20 per cent. of sulphur trioxide is present. Assuming that this sulphate were wholly potassium sulphate, the amount of the latter would be 0.43 per cent.

16. The opalescence produced in lead glasses by means of potassium sulphate is different in character from that produced by potassium chloride. It is less dense, its production by reheating is uncertain, and it is more often produced by slow cooling. Moreover, the intensity of the opalescence does not appear to vary with the amount of sulphate present, at any rate over a range from 0.21 to 0.33 per cent. sulphur trioxide.

17. The actual cause of the opalescence was not investigated. It is conceivably due either to the precipitation of silica through the electrolytic action of the sulphate or to the presence of lead sulphate which becomes insoluble on cooling down to a certain temperature.

18. From the character of the opalescence it is improbable that the potassium sulphate-containing glasses can be utilised commercially in the same way as the potassium chloride-containing glasses for the production of opal glassware.

A Review
of the practical applications of the results of investigations on the "Effect of Chlorides and Sulphates on the Melting of Potash-Lead Glass."

BY

Mr. R. L. Frink, Director of Research.

BEFORE dealing with the results of the investigations on the " Effect of Chlorides and Sulphates in the Melting of Potash Lead Glass," I should like to express my appreciation of the work which has been so ably carried out by Prof. Turner and his colleagues at the Department of Glass Technology, Sheffield. The Reports have treated the subject in such detail that translation of the results to works practice is made easy and should be of great value to the Industry. There are a few points which I believe should be emphasised as from a practical standpoint they might escape the attention or understanding of the glass-maker. Therefore, hoping to broaden the use of this valuable work, I will add my comments.

I believe that this work proves a number of fundamental facts, and also destroys some of the suppositions and misconceptions which have been held regarding the good, bad or indifferent results obtained by the use of chlorides and sulphates as batch constituents. We now have substantial proof that :—

(*a*) Chlorides existing in a glass in excess of 2 per cent. are capable of giving to that particular glass a characteristic opalescent appearance, especially in the case of chloride glasses, on reheating.

(*b*) It would appear that there is a specific temperature range through which opacity can be produced, however, this temperature range will vary with the composition of the glass and the conditions under which the glass is founded.

(*c*) That the presence of an excess of chlorides generally increases the rate of both founding and refining and, up to a certain point, operates to decrease the formation of cords.

(*d*) That under favourable or satisfactory founding conditions the presence of an excess of chlorides with water assists in removing material quantities of iron and should therefore act to stabilize the colour.

(*e*) That the presence of a moderate amount of chlorides increases brilliancy, and if founded under satisfactory conditions assists in various ways in producing a better quality of glass.

The results obtained by adding chlorides to the batch materials so that a quantity of the corresponding element (*i.e.*, of chlorine) would be present to give a calculated quantity (between one-half and one-and-a-half per cent.), confirms the opinion of some old glass makers that the addition of five to fifteen pounds of salt (sodium chloride) to the 1,000 pounds of batch prevents the formation of waves and cords. This procedure seems to have been very successful in the hands of some glass makers, while others have complained that it has been the cause of cords and waviness. These differences in opinion and results in practice can possibly be explained by the results obtained and the conclusions arrived at by the authors of the Reports, for, as has been shown, founding temperatures, conditions obtaining throughout the founding period, amount of moisture present, and also batch mixing probably influence the production of opalescence and cords.

I am of the opinion that, irrespective of how perfectly the batch may be mixed, founding temperatures and conditions that will produce an excessive chemical reaction of certain batch constituents which, when completed, prevent or retard reaction of other constituents, may produce cords, while a lower temperature will permit the retaining of an excessive amount of the electrolyte whether it be chlorides or sulphates, with a result that the retention of electrolytes beyond a certain degree also operates to form waves and cords and to produce opalescence, bloom or clouding. It would seem, therefore, that after one has become acquainted with the furnace operation required to control these factors, the introduction of a specified amount of chlorides or sulphates may be desirable, for it has been shown that in the case of the chlorides when present in excess of $\frac{3}{4}$ to 1 per cent. of chlorine in a lead batch they do not produce opalescence as readily as lesser quantities and they have the advantage of decreasing the amount of volatilisation of lead and other constituents, and increasing the rate of founding. If they are accompanied with certain quantities of moisture the clarification and refining are improved.

Without an accurate analysis of the batch constituents it appears difficult to obtain raw materials which are free, or contain an uniform amount of chlorides and sulphates, it would seem logical to produce an excess of these elements by introducing a definite amount of chloride of sodium or potassium as one of the batch constituents provided the required furnace control can be effected. This confirms the opinions of many old glass makers whose practice it is, after the batch has been mixed, and as it is being charged into the batch wagons, to add by means of a sprinkling can a quantity of salt water. I doubt, however, if the quantity added should amount to more than 2 per cent. of the batch by weight and the salt more than $\frac{1}{2}$ or $\frac{3}{4}$ per cent.

If one considers the founding of glass purely from a heat economy point of view, it would appear that the addition of even small quantities of water would be detrimental, for a

considerable number of heat units must be expended in order to remove this water. However, it is shown by the reports under consideration, and as has been contended by old glass makers, that the presence of a given quantity of water assists to stabilise the colour and the formation of hydrogen chloride, which takes up iron and volatilises it as ferric chloride. Also a more vigorous boil and agitation of batch material would occur, which results in a larger quantity of the batch being exposed to higher temperature than would be if the batch were more quiescent. It is not improbable that the agitation occurring because of the vapourisation of the water also brings all the batch constituents into more intimate relation with each other, thereby effecting more complete chemical reaction. The reports show that the presence of a considerable quantity of moisture somewhat diminishes the tendency to opalescence, and that when moisture amounts to 4 per cent. by weight of the batch materials present, opalescence is substantially prevented. This leads me to consider whether or not the dim, bloom or clouding which is occurring in the ware of a great many manufacturers to-day, particularly where the ware is fire polished, cracked off, or requires remelting of the edges, may be accounted for by the absence of moisture from the batch.

Many manufacturers state that their batch to-day is identical in composition with that in years gone by, but that they now obtain this bloom on remelting, while in the past they were not troubled with this defect. Also, according to several analyses which I have seen of potash which was used 10 or 15 years ago, and that of poorer grades of potash used to-day, I find but very little difference in the quantity of chlorides or in the purity of this ingredient. It is reasonable to assume (and some manufacturers have admitted) that in the past little or no attention was paid to the quantity of moisture that was in the sand or batch materials, and that considerable quantities of water were present.

It therefore seems a not unreasonable assumption that this added quantity of water was responsible for the absence of bloom or clouding, and while it is doubtful if an amount of water equal to 4 per cent. of the weight of the batch existed, it must be taken into consideration that the authors of the reports have performed their experiments on small quantities of batch materials. It is just conceivable that the amount of moisture needed in large scale meltings to eliminate the possibility of bloom is less than in the experimental meltings under discussion, and consequently any quantity of moisture retained in the batch would not disturb the founding to the same degree as in a batch of several hundredweights. It must be borne in mind that it is only within the last few years that much attention has been paid towards the drying of batch materials, and in this matter I am inclined to believe that technologists and glass makers are to-day falling into the error of considering the heat balance sheet, and failing to recognise the importance of, and take into consideration these other factors. The modification of established glass making practices due to theoretical considerations which fail to take into account all these factors is detrimental to the Industry.

The work which has been conducted by the authors relates only to the founding of glass in pots, and therefore the reported results do not consider the effect of "fire" on the quantity of sulphates which remain in the glass. It is a matter of fairly common knowledge and practice, however, that in the making of soda-lime glasses in tank furnaces, the use of a small amount of sodium-sulphate or salt-cake has a very beneficial effect, preventing the formation of scum, termed by some "devitrification," upon the surface of the glass in the melting area of the tank. It also apparently is beneficial in preventing devitrification in the refining end of a tank furnace. So far as I am aware, using such quantities of sulphates that will prevent these conditions does not produce bloom or clouding when fire polishing or glazing the edge of the ware. I assume that the quantity usually

used is too small, and the founding conditions under which the glass is melted, *i.e.*, the reducing atmosphere to which the batch is subjected throughout the melting period, prevent the solution of a sufficient quantity of sulphate to produce bloom or clouding. The usual practice is to use some 10-20 lbs. of salt-cake in a batch consisting of 1,000 lbs. of sand, 400 lbs. soda ash, and 210 lbs. of raw limestone.

Benefit can be derived by using small quantities of sulphate and moisture in the making of soda-lime flint glasses in tank furnaces where selenium is used as a decolorizing agent, particularly where the furnace is operated at a comparatively low temperature and a reducing atmosphere is maintained throughout the furnace. They assist in stabilizing the colour and to some degree prevent its " burning out," and after the proper quantity of decolorizing agent is determined for a given purity of raw materials and conditions of fire, sodium sulphate in conjunction with moisture and borax are beneficial in maintaining the colour constant throughout the annealing of the ware.

Because of the lower opacifying or clouding properties of, and the extreme accuracy required in order to produce any opalescence with, sodium sulphate, and of the several decided and specific benefits which can be obtained by its use in quantities up to 20 lbs. to the 1,000 lbs. of sand, I believe that in melting soda-lime glasses in tank furnaces, its use is to be highly recommended. If and when that degree of perfection and confidence is reached so that the melting of lead glass in tank furnaces be undertaken, I am confident that the presence of small amounts of sulphates will be found beneficial for similar reasons and under similar conditions to those above mentioned. I believe that it will not only operate to increase the rate of melting and refining of the glass, but will also assist in preventing segregation and promote homogeneity.

There is one effect produced by sulphates which has been noted in practice but which has not been dealt with in the Reports, *i.e.*, that in the production of lead crystal glass the

addition of a small quantity of sulphate to the batch gives to the glass a brilliancy and sheen. This possibly accounts for the particular brilliancy and colour obtained by some manufacturers, which others find it very difficult to produce.

It has been quite conclusively shown that a considerable quantity of sulphur trioxide is introduced into the glass through the agency of the gases of combustion, but just how this occurs is as yet problematical. Even when covered pots are used and when there are apparently no means whereby the gases may come in contact with the glass, sulphur trioxide does enter the glass, and therefore it seems reasonable to assume that this occurs through the medium of transfusion through the pot walls or by a process of osmosis, not only through the pot walls but also through the glass itself. As it usually occurs in greater quantities towards the bottom of the pot than at the top, in some instances even to the extent of affecting the colour, it would seem likely that it is introduced at a period during the combustion of the gas or the fuel when the sulphur which is entrained therein is in a state of partial oxidation, this being denoted by the fact that, if analyses be made of the glass at the bottom of the pot and at the top, but little difference in the sulphur content will be found. There will, however, be a pronounced difference in colour between the glass at the bottom and at the top, bordering upon green at the bottom, while perfectly white at the top, which would indicate that a greater quantity of sulphur dioxide permeated the glass at the bottom, while a greater proportion of the sulphur content of the glass at the top was in the form of sulphur trioxide.

All of the work regarding the production of opalescence should be of great value to those manufacturers who produce opalescent ware in the form of " lighting " goods, blown, or pressed opal ware, made directly out of the pot or furnace or that requiring manipulation in the " glory hole " to produce some form of decoration.

While it is quite impossible to lay down any fixed rules concerning temperature in a manner which could be strictly

followed in order to produce a certain definite effect, nevertheless all the figures and data in the reports are of a character which can be easily translated into works practice and conditions. Thus, as has been shown, after meltings have been made over a period of five hours at 1350°C and been allowed to settle and plain down at 1150°C, and after being reduced to a temperature of 900°C and maintained at that temperature for two hours, and again reduced to a temperature of 700°C and maintained for four hours, the glass would be in a condition whereby specific opacity could be obtained. Therefore, if one were to make a trial melt of a glass at approximately 1350°C and subsequently reduce the temperature to approximately 900°C, and again reheat to as low a working temperature as possible, the degree of opacity and the working conditions required to produce a specific character of opacity might be obtained by governing the quantity of chlorine present. In fact, this procedure is being followed by certain manufacturers with exceptionally good results, but only after they have expended large sums of money to determine the necessary conditions in order to obtain specific results. These results have, however, never been published and are held in very close secrecy.

The information that can be obtained justifies a careful study of these comprehensive reports, then by relating the procedure and results obtained to the individual conditions and practice, the glass manufacturer will be amply repaid.

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CONFIDENTIAL TO
THE MEMBERS OF
THE GLASS
RESEARCH
ASSOCIATION.

LONDON
GLASS RESEARCH ASSOCIATION,
50, Bedford Square, W.C. 1.

NOTE.

The Council of the Association does not hold itself responsible for the opinions expressed by the contributors of the various articles.

Contents.

Foreword.

IN addition to the results which are set out in the present Bulletin, a report has been obtained from the Department of Glass Technology, Sheffield, on "The Influence of Water on Rate of Melting and on the Working of Soda Lime Glasses.

It was also hoped to publish the results of the extensive investigations which have been proceeding over the last two years on glass refractories, but in view of further information which will be available, it has been decided to postpone the publication of the reports for a short time.

The experimental stage of the investigations of a commercial method of purifying coal gas for lamp working purposes has been completed, and the plant evolved in our laboratories is to be tested under commercial conditions. It has been thought advisable to delay the publication of the report until the practical applications have been made.

Very considerable progress has been made with the researches on the electrical conductivity of glass, and the results so far obtained clearly indicate that the investigations will lead to very practical factory applications.

R. L. F.

1. Determinations of the Viscosity of Glass. Part 2.

Programme of Researches for 1922.
Ref.: Items 1, 2, *and* 7 (*a*).

Interim Report by the National Physical Laboratory on investigations carried out on behalf of the Association.

MEASUREMENTS of the viscosities of different glasses by means of the method described in our previous Report (see also the Glass Research Association Bulletin No. 2) have been continued. The glasses, which have been supplied by the Glass Research Association, are of various types, ranging from English crystal to very hard gauge glass. As before, heating curves have been taken for each glass, and the temperatures of maximum apparent heat absorption have been compared with the temperatures at which the glasses have a viscosity of $10^{11.95}$ C.G.S. units. It was found, however, that the temperature of maximum apparent heat absorption depends to a considerable extent on the rate of rise of temperature of the specimen. In the case of glass 18, for instance, whereas with a rate of rise of 37.2°C per minute the temperature of the maximum apparent heat absorption is found at 586°C, with a rate of rise of 12.8° per minute, the temperature indicated is 577°C. This result differs somewhat from the statement of Tool and Valasek that change in the rate of rise of temperature produces only minor variations in the temperature found for the apparent heat absorption. Further investigation of the phenomenon is in progress.

The results of the viscosity measurements are shown, separately for each glass, in Figs. 1 to 8, and in Fig. 9 the graphs for all the glasses are superposed, and those representing the earlier series (from our previous Report) are included, for comparison.

Table 1 gives the analyses of the glasses and Table 2 gives the compositions expressed molecularly in such a way that the sum of the figures for soda and potash is always

unity. Although in general the variations of composition are too numerous to admit of ready comparison, the viscosity temperature curves show several instances of great similarity. By changing the origin of temperature by $6\frac{1}{2}$°C the curve for glass 19 becomes practically identical with that for St3, and a further change of $43\frac{1}{2}$°C gives the curve for glass 16. In the same way the curves for glasses 10 and St7 differ by 3° and for glasses 18 and St59 by 51°. The glasses 10 and St7 are of the same general type, but as regards the other glasses the similarities in the shape of the viscosity curves are accompanied by large differences of composition. Such a result is somewhat surprising in view of the number of independent variables involved. It is further interesting to note that the apparent difference in "working range" between these different glasses would seem to be merely a question of the actual temperature at which the glass attains the degree of viscosity which renders it workable. The actual range of temperature within which the glasses are workable would not, from the present results, be expected to vary much between a hard and a soft glass, but for the hard glass the whole range lies at a higher temperature. This involves much quicker cooling during working, so that although the working range when expressed as an interval of so many degrees Centigrade may be nearly the same, the range as expressed in the time during which a given piece of glass cools through the working range may be widely different, and always shorter for the harder glass. The harder glasses might, however, be expected to have working properties very similar to those of the soft ones if it were possible to work the former with a hotter flame and surrounded by a heated enclosure so as to produce rates of cooling equal to those which occur at the lower temperatures at which the softer glasses are worked. The glass 17 is remarkable, as it is the only one showing an exact exponential variation of viscosity with temperature. It will also be noticed that in spite of the exceptional hardness of this glass its working range is unusually long. This may be largely due to the high ratio of silica to bases in this glass.

TABLE I.

	9	10	11	15	16	17	18	19	20
SiO_2	52.54	65.96	67.60	66.22	66.78	69.82	66.26	63.26	70.72
Al_2O_3	0.34	4.98	3.40	7.10	9.70	5.34	5.48	3.44	1.86
Fe_2O_3	0.38	0.78	0.26	0.48	0.50	0.54	0.64	0.20	0.26
MnO	0.16	0.10	0.10	0.38	0.36	—	—	0.24	0.16
CaO	0.30	6.04	6.24	6.40	0.40	8.30	0.42	0.74	13.78
MgO	0.15	0.93	0.34	0.28	—	0.48	—	0.27	0.41
Na_2O	0.18	15.74	14.24	15.46	13.38	3.69	11.66	9.10	12.40
K_2O	12.10	5.72	0.18	3.46	0.30	2.06	0.30	0.98	0.30
B_2O_3	—	—	2.28	—	8.54	4.48	7.91	20.78*	—
ZnO	—	—	5.59	—	—	—	7.30	—	—
Sb_2O_3	—	—	—	—	—	—	—	0.99	—
BaO	—	—	—	—	—	5.48	—	—	—
PbO	33.82	—	—	—	—	—	—	—	—
	99.97	99.85	100.23	99.78	99.96	100.19	99.97	100.00	99.89

* By difference.

TABLE II.

	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	Na_2O	K_2O	B_2O_3	ZnO	BaO	PbO	Sb_2O_3
9 ...	6.646	.0251	.0183	.0175	.0411	.0281	.0221	.9781	—	—	—	1.152	—
10 ...	3.467	.1547	.0076	.0044	.3422	.0731	.806	.193	—	—	—	—	—
11 ...	4.84	.1437	.0069	.0060	.480	.0362	.991	.0082	.1406	.296	—	—	—
15 ...	3.84	.2427	.0105	.0189	.399	.0241	.871	.1285	—	—	—	—	—
16 ...	5.06	.433	.0141	.0233	.0324	—	.9854	.0146	.557	—	—	—	—
17 ...	14.21	.642	.0418	—	1.82	.1460	.731	.269	.786	—	.440	—	—
18 ...	5.75	.2804	.0209	—	.0392	—	.9833	.0167	.591	.469	—	—	—
19 ...	6.659	.2139	.0825	.0216	.0838	.0425	.933	.0667	1.882	—	—	—	.0216
20 ...	5.77	.0896	.0079	.0113	1.211	.0502	.9842	.01576	—	—	—	—	—
St59 ...	3.574	.1371	.0045	—	.363	.0866	.808	.1919	.0149	—	—	—	—
St 7 ...	3.71	.1720	.0034	.0024	.431	.0158	.7598	.2402	—	—	—	—	—
St 3 ...	4.01	.1847	.0054	.0051	.462	.0340	.6856	.3144	—	—	—	—	—
St68 ...	3.894	.237	.0064	.0148	.378	.0350	.892	.1089	.0551	—	—	—	—

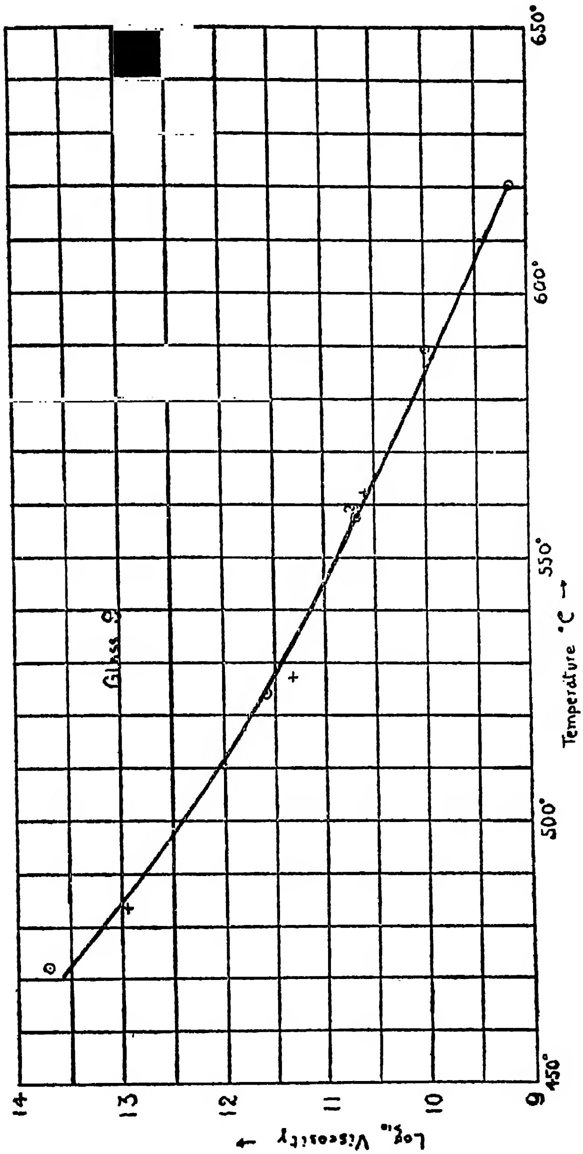
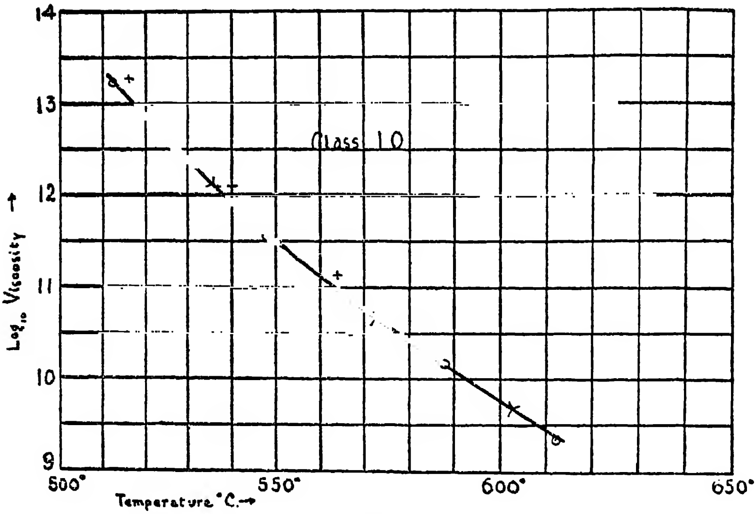
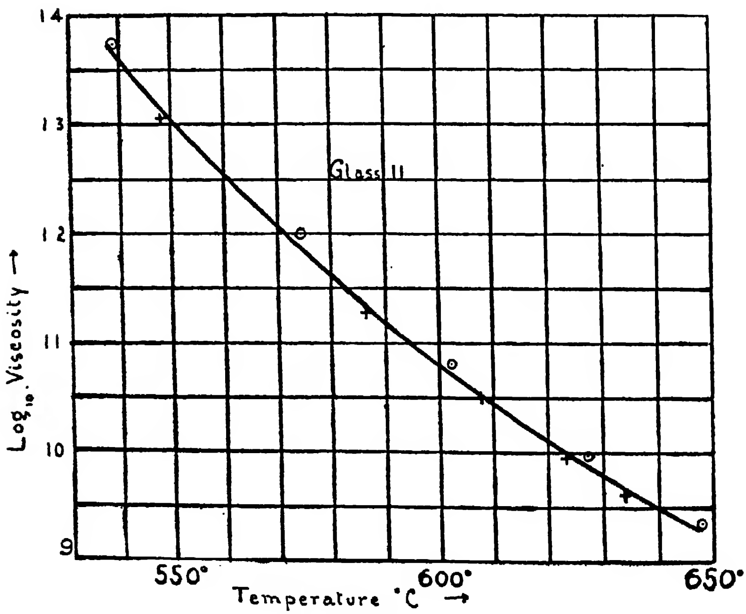

Glass 9
14
13
12
11
10
9
Log10 Viscosity →
450°
500°
550°
600°
650°
Temperature °C →

FIG. 1.



14
13
12
11
10
9
Log.10 Viscosity →
500°
550°
600°
650°
Temperature °C →
Glass 10

FIG. 2.



14
13
12
11
10
9
Log.10 Viscosity →
550°
600°
650°
Temperature °C →
Glass 11

FIG. 3.

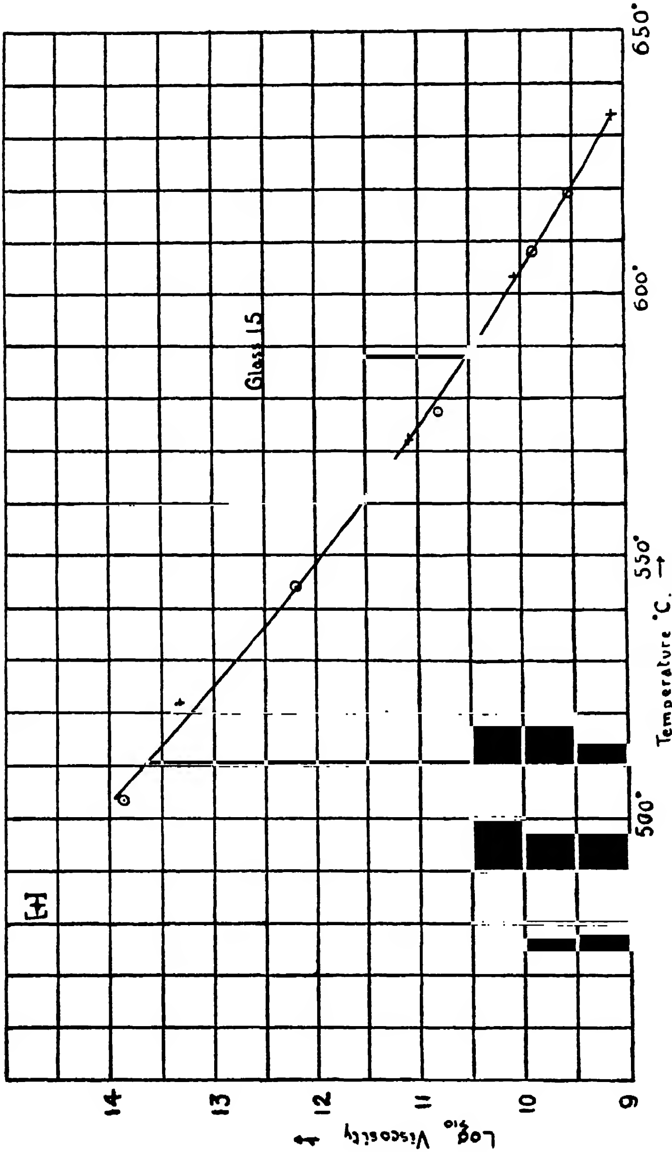

Glass 15
650°
600°
550°
500°
Temperature °C →
14
13
12
11
10
9
Log10 Viscosity →

FIG. 4.

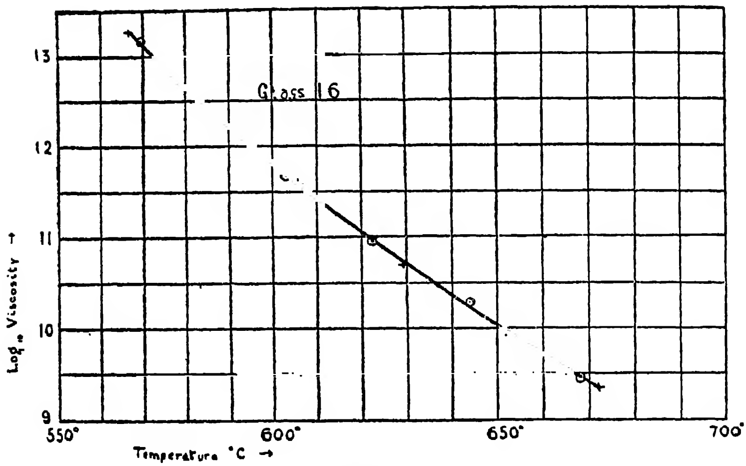

Glass 16
13
12
11
10
9
Log₁₀ Viscosity ↑
550°
600°
650°
700°
Temperature °C →

Fig. 5.

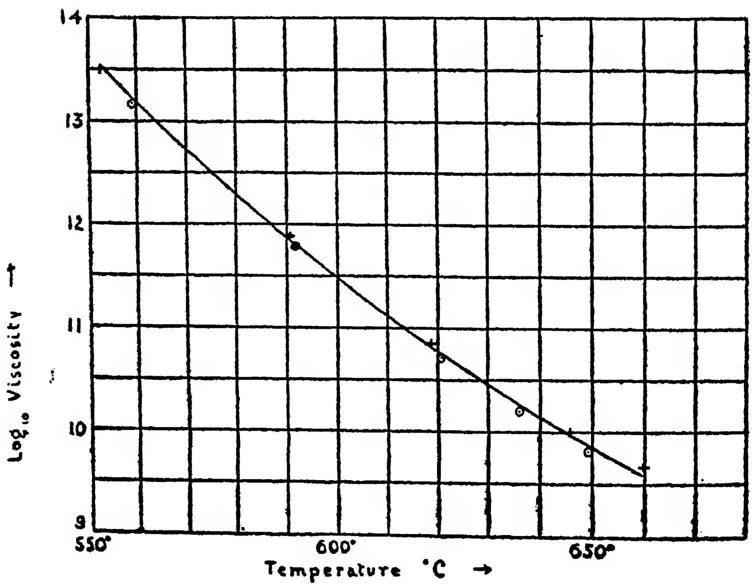

Glass 18
14
13
12
11
10
9
Log₁₀ Viscosity ↑
550°
600°
650°
Temperature °C →

Fig. 6.

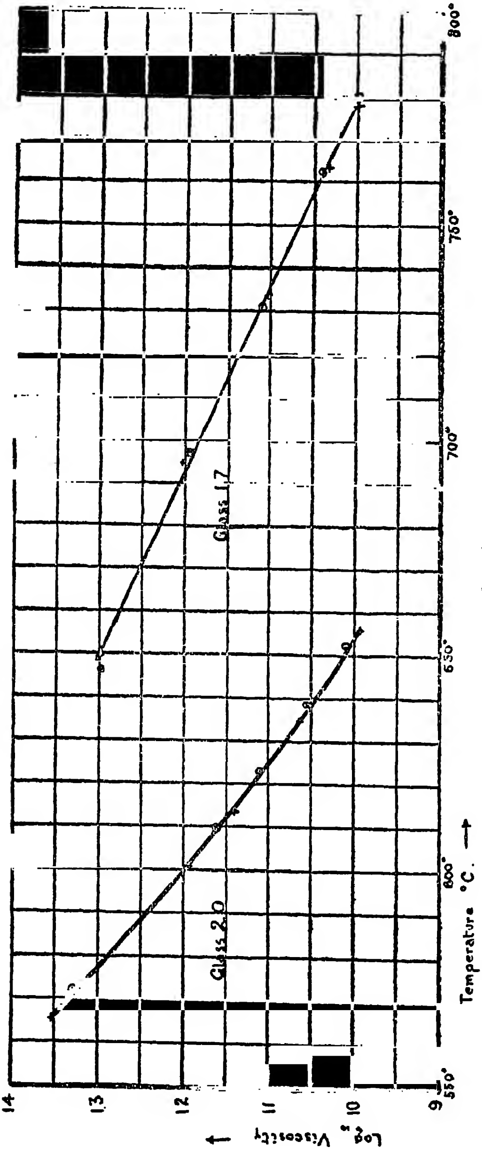

Glass 1.7
Glass 2.0
14
13
12
11
10
9
550°
600°
650°
700°
750°
800°
Temperature °C. →
← Log_e Viscosity

FIG. 7.

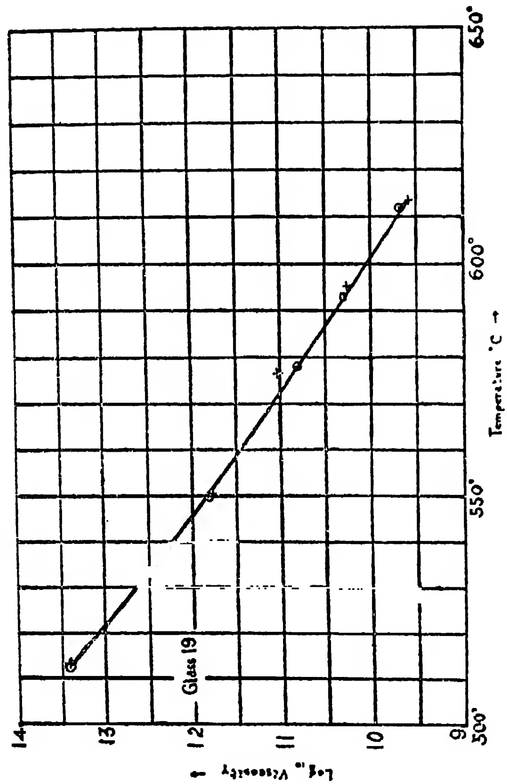

Glass 19
14
13
12
11
10
9
500°
550°
600°
650°
Temperature °C →
← Log₁₀ Viscosity

FIG. 8.

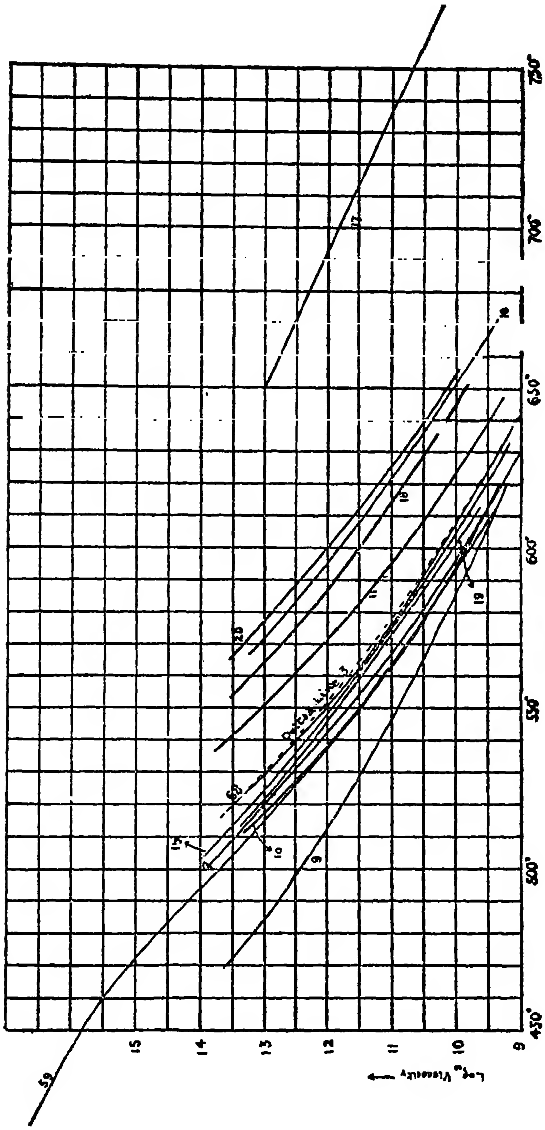


Fig. 9.

II. A New Mould for Turned Ware.

(A Report of Investigations carried out by Mr. N. B. Mattingley.)

THE object of this research has been to obtain a mould for turned ware which would not require continual pasting.

Up to the present time it has been customary to use metallic moulds, usually made of iron, copper or like materials, the inner surfaces of which are coated with a paste composed of mixtures of graphite and oil, or charcoal and oil or wax, which on heating furnishes a semi-charred graphite or carbon coating on the aforesaid inner surfaces. This method of preparing the inner surfaces of the moulds by the production of a special coating thereon entails several disadvantages, chief amongst which is the expense incident to the maintenance and upkeep of the coated moulds owing to the shortness of their useful life, which may be a matter of less than one hour.

Investigations have been conducted towards the production of a metal which is vascular, the vascularity or very finely pitted surface to extend into the body of the metal, but not necessarily throughout the entire thickness of it, so that this surface would allow of the absorption of gases or liquids to take place for some depth into the body of the metal; then when the surface of the metal be heated the substance contained in the pores or vascules of the metal will expand to the surface and form a film over the surface.

Investigations were commenced on aluminium alloys. It was found that a certain alloy gave a very porous metal, these pores being brought to a satisfactory state by chemical treatment. (Fig. 1 shows the metal before treatment and

FIG. 1.

FIG. 2.

Fig. 2 shows a mould made from this alloy which has been chemically treated.)

A small cup shaped mould was first made so as to find out the exact effect produced on the glass. During this trial water was used to effect the film between the glass and the metal. The results from this experiment led to the making of a beaker mould for trial in a factory. Water and air were tried at first as fillers for the pores. A certain measure of success was obtained by dipping the mould in water between each successive blowing, but much better results were obtained by using a composition consisting of resin, beeswax and linseed oil. With this filler a trial run was made, and out of 913 samples blown, 26 were rejected for scratches and 66 for being badly blown; that is to say, they were not cylindrical. The latter fault has been remedied to a large degree by varying the method of blowing; and the cause of the scratches, probably due to dust or tiny particles of glass from the " burst off " entering the mould, was eliminated by wiping the part affected with a damp rag. The mould was used continuously through the shift of 8 hours, and no break had to be made for the cooling of the mould. At the end of the turn, the mould was put away, until the next time for using it, when it was brought out, heated up by putting some hot glass into it, and work was started right away, no re-filling of the mould being necessary.

At this stage it was necessary to find some economic method of manufacture of this metal which could be applied commercially. Further research resulted in the production of an alloy which had a constant composition, and it was found that the porous mould alloy could be obtained equally well by adding the required quantity of this alloy to a given quantity of aluminium. It may be mentioned here that the alloy used for these moulds has been remelted and recast without its having lost any of its porosity.

The beaker mould which was first tried was not of the standard shape used, so it was decided to cast a beaker mould to the patterns supplied by the firm at which these

experiments were being carried out. This type of mould was worked on a foot machine. Out of 396 beakers blown, 5 were rejected for mould marks and 38 for scratches on the ware. The so-called mould marks were a series of pimples on the surface of the mould, being caused probably by the mould being too cold or the blower having stopped turning the metal in the mould while blowing. An experiment was carried out to find through what range of temperature the mould could best be worked, and it was found that if one glass blower used the mould, it kept at a fairly constant temperature, between 300° and 350°C. Aluminium loses its heat rapidly (*i.e.*, more rapidly than an iron mould would do), and so keeps at a more constant temperature. The mould was next worked with two glass blowers at the quickest speed obtainable so as to arrive at a temperature at which the mould would cease to work (that is, when it would become difficult to turn in), the rate of blowing being about one every 15 or 20 seconds. When the temperature reached 465°C it was difficult to turn the glass in the mould. It has been found that the correct temperature can be maintained if one mould is used per glass blower at an average rate of blowing of roughly one per minute or 50 seconds.

The mould just referred to is now in constant use. Other moulds have been made, including a funnel mould, which was put into operation with soda metal. Out of 600 funnels blown, 589 were accepted by the Inspection Department as satisfactory, the others being rejected for bad metal, uneven blowing, etc. Nearly twice as many funnels were blown in this mould as compared with the iron mould used, for compulsory rests have to be made roughly every $\frac{3}{4}$ hour for cooling and re-pasting. This means a delay of 15 minutes, or of $1\frac{1}{2}$ hours during the shift, representing the loss in blowing of about 50 to 60 funnels per shift.

Another mould which has been made is for a gas container of about 1/12th cu. ft. capacity to be used in conjunction with a gas apparatus. The ware from this mould has turned out to the firm's satisfaction.

Experiments are now being carried out with ware from lead glass, that is, for tumblers and electric light bulbs. Footboards for making the feet of wine glasses have also been made. The question of expense of these moulds has been carefully borne in mind, and although the initial cost of the metal per pound it more expensive than iron, the quantity of metal required would be about a third as much, also the cost of machining a mould should be nearly half that of an iron mould.

III. Notes

on the Use of Stack Draught Gauge, Gas Pressure Gauge and Flue Gas Pyrometer in the Control of Glass Furnaces.

BY

V. E. H. EVANS and C. SCHOFIELD.

PROBABLY the greatest waste in the modern glass-house occurs through inefficient production and utilization of the fuel consumed by the furnace.

To obtain efficiency it is absolutely necessary for the manufacturers to know how—

(1) To produce the best gas, and supply it to the furnace at a constant pressure.

(2) To assure the proper admixture of preheated air and gas for combustion.

(3) To assure perfect and complete combustion in the founding zone.

(4) To withdraw the products of combustion from the furnace in a proper manner.

A pyrometer indicates with fair accuracy the temperature in any particular zone in which it may be "sighted," but does not afford any indication of the degree, rate, and perfection of combustion.

The importance of founding conditions cannot be over-estimated, and no effort should be spared to collect all available data on this point. Generally it is the practice to sight a pyrometer in the founding area, and usually this is located in the end wall of the furnace by the charging hole. The inefficiency of such installation is apparent when we remember the varying conditions to which this zone is subjected. Batch is fed on at frequent intervals; piles assemble below

the pyrometer tube; dust settles upon it and prevents the correct recording of even local temperature. It is obvious, therefore, that no reliance whatever can be placed upon a pyrometer in the melting area, for other than purely relative local conditions, and no use can be made of dampers and valves to obtain efficient furnace control from the information which it supplies.

The Glass Research Association, with a view to overcoming the discrepancies in founding, have made many investigations and have evolved two instruments, which, in the hands of a competent furnace operator, ensure efficiency and economic furnace operation.

Fig. 1 is a reproduction of the Draught Gauge. The instrument is actuated on the gas balance principle. The black container (A) is partly filled with water. A pipe (B) is led from the flue and connected to a short length of pipe which runs through the container (A) to a position just above the water level. The bell (C) is in position over the pipe opening, the water thus forming a seal. As the draught increases or diminishes the bell is lowered or raised in the water. Connected to the bell (C) is a fulcrum arm (D) which records upon a 6″ 24 hr. chart the exact draught in inches of water pressure. By means of the counter balance weight (E) adjustments can be made, and the whole chart can be used for either 1″, 2″ or 4″ of water. Fine adjustments are made by means of the knurled screw (F).

The gas pressure gauge is made on a similar principle, but records pressure instead of draught.

Both of these instruments are enclosed in dustproof cases with a glass front and can be procured either from the Glass Research Association or the makers, Messrs. Negretti and Zambra.

The gas pressure gauge furnishes the producer man with information as to the pressure with which he is supplying the gas to the furnace and the uniformity of producer operation, and is a means of spurring him to his best efforts to maintain

such uniform conditions. It thus tends to eliminate the strife between furnace man and producer man, safeguarding the one when the other is to blame for a cold furnace, and furnishing the manufacturer with evidence should the years' old battle be revived.

It also furnishes much valuable information as to the time of poking, charging, etc., so that the manufacturer has again evidence to hand with which to confirm or deny an argument should occasion arise.

If in addition to this gas pressure gauge the draught gauge, together with a Pyrometer, is installed in the stack flue, there will be at the disposal of the furnace operator a method for obtaining the perfect efficiency for which he is aiming in an economical manner. The draught gauge and flue gas Pyrometer afford him valuable information as to the volume and temperature of the products of combustion escaping up the stack. In addition to this, in a regenerative furnace, it records the exact time of reversals. Should there be a constriction in the flues, or a fall of checker work or rider arches, etc., this will be immediately revealed. If the exact location of this cannot be determined from the instrument in its permanent position, it is only necessary for the furnace man to temporarily disconnect it and, working towards the furnace, make openings in the flue at various points, sufficiently large to admit a piece of ½″ pipe, to which the instrument is connected and readings taken. Points will be reached where there is a great disparity in draught, and between these points the obstruction or constriction will be found.

Since the intake of secondary air for combustion is dependent to some extent upon the stack draught, it follows that the best draught line will be one which will supply sufficient air for complete combustion and remove the gases when they have given up their heat. In no case should the gases passing the flue pyrometer record a greater temperature than 500°C, this, of course, being governed by the distance of the stack from the furnace. It will, however, be

realized that the checker work also has considerable influence upon the flue gas temperature. Insufficient height or tonnage of brick in the regenerators will have the effect of raising the flue gas temperature, with a consequent loss in efficiency.

Another point having considerable influence upon the temperature of the regenerators is the period of reversals. Should the period be too long, available heat will be wasted, and should the period be too short, the fullest value will not be extracted from the products of combustion. According to the amount of checker work used the period of reversal is determined, which should never exceed 30 mins. and preferably 20 mins., and this should be strictly adhered to. Unequal reversing of the furnace results in the superheating of one regenerator and the consequent cooling of the other, which has the effect of causing an unbalanced condition within the furnace which detracts from efficiency and is contributary to formation of stones and seed. A glance at the draught chart will reveal whether the furnace man is correctly reversing the furnace, and whether the furnace is balanced.

It is impossible to lay down any definite rules as to the correct draught, gas pressure, and flue gas temperature required for a specific furnace, as no two furnaces are constructed alike. Having made the installation, however, a few careful observations and adjustments will soon reveal the correct " lines " required for the aforementioned perfect conditions.

Generally it will be found that adjustments act in the manner indicated as follows:—

Raising the stack damper will show an increase in draught, a possible decrease in gas pressure, an increase in flue gas temperature, and a consequent drop in furnace temperature.

An increase in gas pressure will show a decrease in draught, and increase in flue gas temperature, with a possible decrease in furnace temperature.

Raising the stack damper, and proportionate opening of the air valve and gas damper, will show a constant draught with a decrease in gas pressure, a constant flue gas temperature, and an increase in furnace temperature.

Opening the air valve will show a decrease in draught, a decrease in flue gas temperature, and a possible decrease in furnace temperature.

The effect of damper adjustments and other fluctuations will readily be seen by a comparison of charts 2a, b and c.

From 10.30 a.m. until 1 p.m. was a period of cleaning fires or burning out period. The time lost to the manufacturer during this process is *clearly* indicated.

At 1 p.m. production was again resumed, but ideal conditions did not obtain long. Apparently by an oversight the furnace man forgot to reverse at 2 p.m., and did not discover his mistake until 2.15 p.m. This caused an unbalancing of draught and flue gas temperatures, and it was not until 4 p.m. that he rectified the error. This is clearly indicated upon the chart.

At 6.15 p.m. the stack damper was raised, causing an increase in draught and an increase in flue gas temperature.

Again at 9.30 p.m. the furnace man omitted to reverse, but this time he did not reverse again until 10 p.m. His method of restoring the balance of the furnace proves very interesting, and is very clearly defined on the charts.

Between 1 p.m. and 4 p.m. the furnace was again unbalanced, due probably to an air leak or constriction in the flues.

From 4 p.m. until 9.30 p.m. was very windy and the effect upon the draught is clearly defined.

The pressure and efficiency of different types of producers is interesting. On Diagramatic Chart 3 illustrated are three typical readings obtained from different producers,

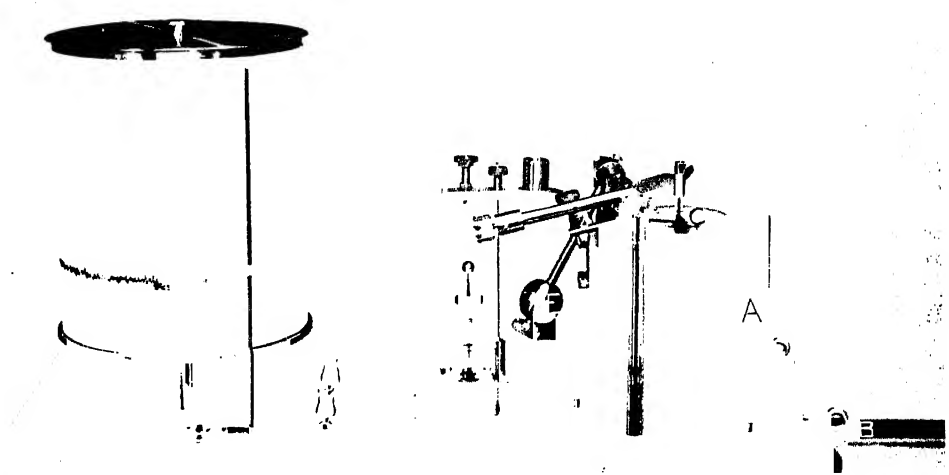


FIG. 1.

FIG. 2A.

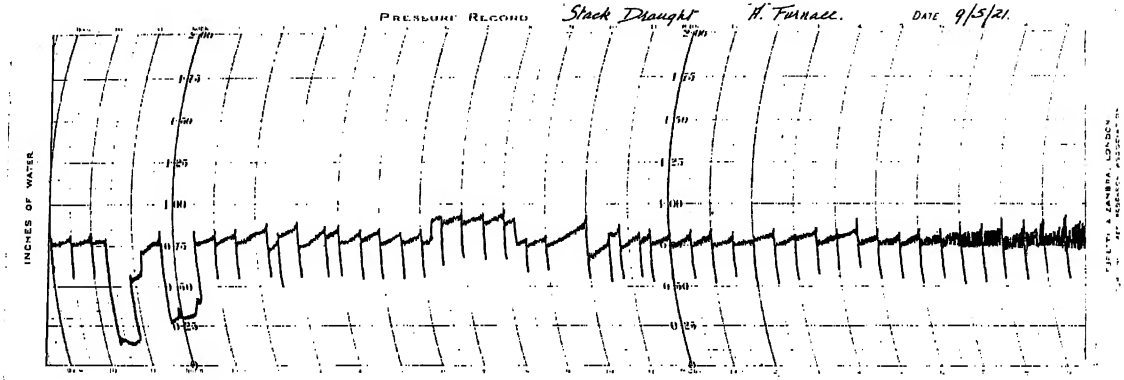

PRESSURE RECORD
Stack Draught
"A" Furnace.
DATE 9/5/21.
INCHES OF WATER
2·00
1·75
1·50
1·25
1·00
0·75
0·50
0·25
0

FIG. 2B.

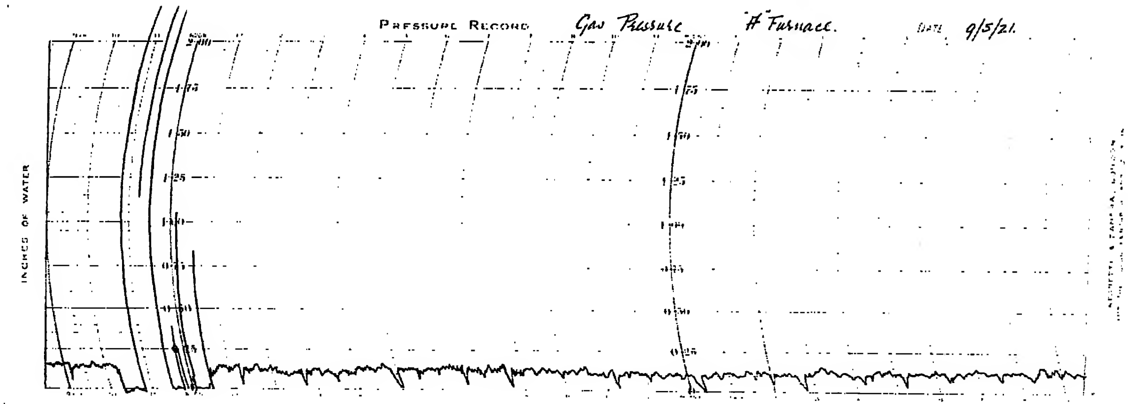

PRESSURE RECORD
Gas Pressure
"A" Furnace.
DATE 9/5/21.
INCHES OF WATER
2·00
1·75
1·50
1·25
1·00
0·75
0·50
0·25

FIG. 2C.

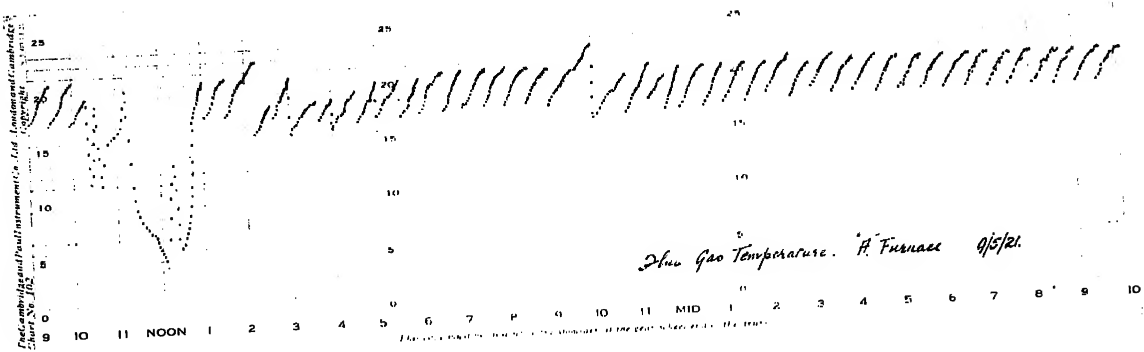

Flue Gas Temperature. "A" Furnace 9/5/21.
9
10
11
NOON
1
2
3
4
5
6
7
8
9
10
11
MID
1
2
3
4
5
6
7
8
9
10

FIG. 3.

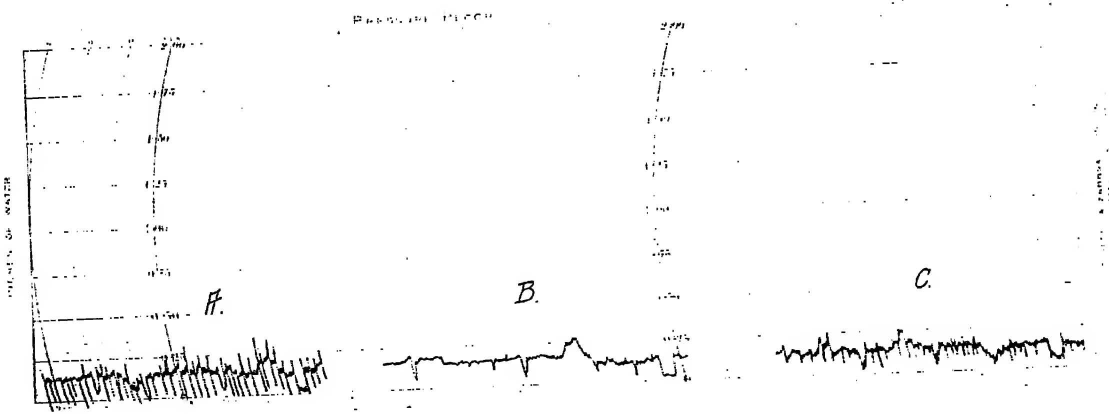

A.
B.
C.

Chart No. 3.—(A) This is a typical record as obtained from a producer such as the Kerpley, having a mechanical grate, but no automatic feed or agitator.

It will be noted that the general line is intersected by a number of vertical lines. Each of these lines indicate the dropping of a hopper of coal, so it is possible to compute with fair accuracy the quantity of coal used and the times of charging. At 10 a.m., 11.15 a.m., 1 p.m., and 3 p.m. a sudden drop in the line will be noticed. This is due to agitating.

(B) Record as obtained from a producer having a mechanical feed and agitating device. In this instance the dropping of clinker is indicated by a sudden fall in pressure which will be noted at 5.40 p.m., 8.15 p.m., 10.50 p.m., and 11.25 p.m.

(C) Record as obtained from an ordinary hand fed and poked type of producer. The charging and poking lines previously referred to are again indicated. The erratic production of gas from this producer is very much in evidence.

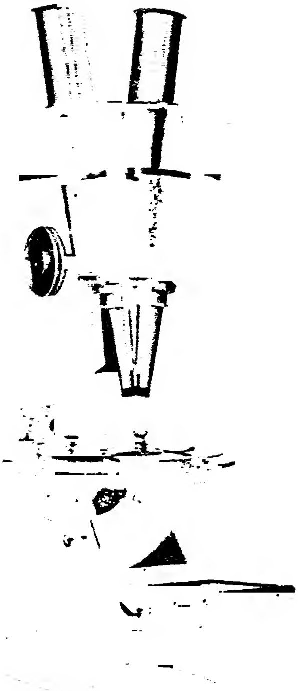
Fluctuations in the general curve of A and B are due to the steam pressure and condition of the fuel bed in the producer.

IV. The Use of Polarising Apparatus with Greenough Binocular Microscope for Study of Glass.

THE following article is primarily written to introduce the use of polarising apparatus with Greenough Binocular Microscope to glass manufacturers who have heretofore not considered the advantages obtained by using such an instrument in their works. At the same time, it is hoped that those who are already equipped with a microscope will find this new model of considerable value when examining batch ingredients and imperfect glass in the factory. Everyone associated with glass manufacture is aware of the difficulties which arise in producing good metal, and frequently considerable proportions of ware made are rejected for inclusions of foreign particles of a non-vitreous nature appearing in the metal, known as stones and devitrification. Cords are another source of trouble and are often so prominent as to render the ware unsaleable. In order to minimise losses in production from these and similar imperfections it is essential that a proper identification of their type and source be determined in the shortest possible time. Chemical analysis may be used, but this method is generally lengthy and many hours may elapse before any satisfactory information is forthcoming, whereas a microscope near at hand in charge of a person well trained as to its use enables speedy determination to be made by the measurement of distinctive optical properties.

Microscopes which are to be continually used in glass-works must be rigidly constructed and as far as possible free from delicate mechanical parts which soon become worn and out of adjustment unless carefully handled.

The preparation of thin sections for microscopic examination is expensive and considerably increases the time spent in making a diagnosis; therefore, it is a distinct advantage



to view stereoscopically, inclusions in glass and grains of batch which possess appreciable amounts of depth. With this method of observation the impression of solidity is obtained by viewing the object from two different aspects which are combined by the action of the two eyes. Not only does binocular vision give stereoscopic relief, but also improves the constancy of the perceptive faculties by resting the eyes and preventing fatigue during prolonged observations.

The following is a brief description of a binocular microscope which at the suggestion of the Director of Research has been converted into a petrological model by the addition of a polarising attachment, at the same time giving all the advantages of stereoscopic vision.

The instrument which is of the Greenough type consists of two juxta-positioned microscopes complete in themselves, each possessing its own objective, and by the incorporation of a Porro prism erecting system to which the two bodies are attached, the object is viewed in an erect position, and with a true stereoscopic effect. Sufficient latitude to accomodate variations of interpupillary distances is provided, and readily effected by the rotation of the prism boxes which move with a lateral motion. The microscopes are simultaneously raised or lowered by the use of a long range of coarse rackwork, fine adjustment not being required.

The base and pillar is the horseshoe pattern, rigid in construction, making it possible to move the limb to which the microscopes are attached, backwards, without any danger of the instrument falling over. For the convenience of the observer when in a sitting position, an inclining joint is fitted to the stand which permits the microscopes being tilted to any angle up to 45°.

As already stated, it is necessary with this type of microscope to have two objectives accurately paired, and these are mounted on a dove-tailed slide to facilitate changing from one power to another. Four sets of these objectives are

made with focal lengths ranging from 54 millimetres to 27 millimetres, and are all interchangeable. Each pair of objectives are adjusted to superimpose the two images by moving the axis of one relatively to the other with three small set screws which holds them to the slide. The microscopes are delivered with the objectives adjusted and it should not be necessary to have to alter them if a little care is exercised in their use.

The Huyghenian eyepieces are supplied in pairs, numbered 1, 2, 3 and 4 with initial magnifying powers of 5, 6, 8 and 10 diameters respectively. One of each type of eyepiece is fitted with cross wires with the exception of the No. 2, which has a graticule ruled with squares for counting fragments or grains of material in a certain area.

For the purpose of observing the phenomenon of double refraction in crystals and strained glass, a polarising attachment is fitted to the microscope, the light being polarised by reflection from a black glass plate placed just beneath the stage at the angle of polarisation, which is approximately 57½ degrees. The black glass plate or mirror is illuminated by an auxiliary silvered mirror adjustable to any angle, and attached to the mount of the first by a movable arm which permits movement up and down. This type of polariser was adopted on account of its cheapness, as a Nicol prism of considerable aperture would be required to allow equal amounts of light to pass to each microscope. Two small analysers of the Nicol prism type are used, each being mounted just above the objectives and set to give extinction wit.. the polariser. The stage of the microscope is so arranged that it may be rotated and the amount of rotation determined by means of a graduated scale and vernier, reading to minutes. The function of this is to separate anisotropic crystals from those that are isotropic, which is accomplished by rotating them under polarised light. Isotropic substances present no change in the appearance of the field on rotating the stage, the light travelling through them with equal ease. With anisotropic substances in which the velocity of the transmission of light differs in different direc-

tions, the field will alternately change from light to dark four times during one revolution. The graduated scale on the bevelled edge of the stage is used for measuring the angles of extinction and also the cleavage angles of crystals. For the purpose of determining tension and compression strains in glass which are of low birefringence, a mica wave plate is provided and housed under the stage in a rotating cell attached to an arm for swinging it in and out of the field.

A substage condenser is not needed, sufficient light being obtained to illuminate the object from daylight or 100 candle power half watt lamp with a suitable diffusing screen in front. When using artificial light, the lamp should be placed close to the adjustable mirror so as to insure equal illumination in both microscopes. When viewing objects by transmitted light the polarising plate is removed from the groove holding it in position, exposing a silvered mirror which reflects the light received from the illuminating mirror on to the object.

To explain the construction of a microscope is no criterion as to its value in glassworks without giving some information of the methods adopted in carrying out investigations, so the following will be devoted to this project.

The identification of an object by microscopic examination is accomplished either by observing its structure and comparing it with a known object of its kind, or by the measurement of definite optical properties peculiar to itself. Therefore, these methods can be applied to the testing of batch ingredients for impurities and to the identification of imperfections in glass, especially if they are crystalline.

Let us consider the microscopic examination of sand, which is used as the principal source of silica in glass making. Sand consists of broken grains of crystalline quartz associated with a considerable number of heavy mineral impurities, many of which are detrimental to producing a white metal. If a small quantity of sand is mounted on a slide in a medium such as Canada balsam or oil of cloves and examined by transmitted light, the following will be observed: the variation in the size of grains; the angularity

of the grains; the transparency, turbidity or opacity of the grains. When examined by reflected light some of the grains will be pale amber colour, others dark brown or even black, while the remainder will be composed of water-clear quartz. This staining of the grains is due to a coating of iron oxide on the quartz, and the darker grains may be ilmenite ($FeTiO_3$), magnetite (FeO_4) or other harmful minerals. Microscopic analysis of sands can only be accomplished by petrologists who have made a study of rock forming minerals, but on the other hand it is possible for anyone to compare one sand with another and state definitely whether they are both of the same standard of purity. For example, a manufacturer obtains a supply of sand from a certain pit, and knows from chemical analysis that its iron content is within the limits necessary for producing a certain colour of metal. Therefore, if a selected sample of the analysed sand is taken and mounted on a slide a standard has been made against which future supplies from the same pit can be compared to see whether they fall below the quality of sand demanded by the glass. On examining the standard slide under the microscope by transmitted light it will be seen that the grains of pure quartz are only just visible, because of the close similarity in refractive indices between the quartz and the mounting medium. The ferruginous coating on the grains is then easily detected by their amber colour, and the heavy detrital minerals stand out in relief, often appearing quite opaque. Felspar has practically the same refractive index as quartz, but is usually detected by its turbid appearance. By using the eyepieces fitted with the squared graticule already mentioned, it is possible to count the number of grains of each condition in a certain area, thus classifying the quality of different consignments of sand by comparison with a standard. Three or four selected samples from a truck load of sand, although only a small representative of the bulk, will be sufficient either to pass or condemn it, and the whole operation can be carried out in the space of a few minutes. By mounting the standard under one-half of the cover glass only and leaving the other half blank so that the sand to be tested can be floated under with a medium such as

oil of cloves, the two can be viewed in the field of the microscope at the same time. This method is of considerable assistance to the observer, but a great amount of care must be exercised not to spoil the standard by breaking the cover glass when cleaning out the sand under test. A series of standard slides prepared in this way with iron contents varying by .04 per cent. permits a quantative estimation by comparison to be made of each consignment of sand. The mineral impurities in sands are identified by examining their optical properties, such as refractive index, extinction angle, birifringence, etc., but it is not within the scope of this short paper to deal with these characters, neither is it necessary when comparing sands with a standard to know them.

Crystalline bodies in glass such as stones and devitrification may be identified by microscopic examination, which renders possible the measurement of their refractive indices and other optical properties. In all cases the stones are opaque in the bulk and must be crushed up into fairly fine fragments to permit light being transmitted through them. The Becke method is used to determine their refractive index by placing a small quantity of the crushed stone on a slide, and immersing in an oil, the index of which is measured on a refractometer. For workshop methods only one liquid is necessary, such as oil of cassia, which has an index of about 1.60 and can be used in all cases where the index of the glass does not exceed that of the liquid. Refractive indices can only be determined when the boundaries of the fragments under examination against the liquid in which they are immersed have completely disappeared. Usually sufficient information is obtained by ascertaining whether the index of the crystal is higher or lower than that of the medium against which they are examined. This is determined by focussing up the fragments sharply under the microscope, and on raising or lowering the tube very slightly it will be found that the boundaries of the fragments are marked with a band of light appearing either on the inside or the outside of them. On raising the tube the band will move towards the substance with the higher refractive index; thus if the band moves

within the fragment then its index is greater than that of the liquid, and *vice versa* if the band moves in the opposite direction.

The microscopic determination of stones depends upon the fact that sillimanite, which is a characteristic of clay stones, has a refractive index of 1.67, considerably above that of oil of cassia mentioned above, whereas tridymite and cristobalite, which are the main constituents of batch stones, have indices of 1.47 and 1.48 respectively. It should be noted, however, that tridymite may occur with sillimanite in clay stones, and consequently the latter substances must be sought for carefully before a true diagnosis is possible.

When the black glass plate is inserted and the fragments of crushed stone examined under polarised light, a check can be made on the results derived from the refractive indices tests by observing their amounts of double refraction. Sillimanite has a very high double refraction and can be readily picked out by its brilliant colours, while tridymite and cristobalite have low birifringence and present only different tones of greys, rarely showing any colour at all. In some cases when examining batch stones, fragments of quartz will be found remaining from the undigested sand and will show fairly brilliant colours under polarised light, but these can be identified by their refractive index, which is approximately 1.55.

Many other uses can be found for microscopes in glass-works, such as the examination of cordy glass, which has been dealt with in Bulletin No. 2. Blisters, seeds, and refractory materials are also included, and suitable methods of examining these will be communicated in a future report.

V. The Influence of Moisture on the Mixing of Glass Batches.

Report by the Department of Glass Technology, University of Sheffield, on Investigations carried out on behalf of the Glass Research Association.

IN many glass factories, especially those engaged in melting glass in pots, some means of drying the sand and in some cases even of calcining it before use, is regarded as a necessary essential of the factory equipment. Several books on glassmaking advocate the drying and calcining of sand, and there are certainly at least two excellent reasons for doing so, namely, the economy of buying dry instead of wet sand, and the greater ease with which the dried material can be weighed out or measured.

The same remarks apply with equal force to the other constituents of the batch.

The Possible Effects of Moisture.

In looking at the problem in a general way, several possible effects of moisture can be recognised. We shall include, for the moment, other effects than those which moisture may have on the mixing only.

In the first place, from the strictly chemical point of view, it is probable that reaction would not take place at all unless a certain minimum amount of moisture were present. In practice, however, this case does not arise, since ordinary dry materials still contain far more moisture than is necessary to set chemical reaction in operation by the intervention of the catalytic agent, assuming such action to be operative in glass melting.

In general, therefore, the effects of moisture may be :—

(1) To cause adhesion between the particles.

(2) To combine chemically as water of hydration with batch ingredients, such as soda ash and saltcake, causing them to cake.

(3) To be absorbed by deliquescent materials, such as sodium nitrate, which does not actually combine with the water.

(4) To keep the batch temperature at a low level in the furnace until the moisture has been volatilised.

(5) To be a source of danger in increasing the tendency of pots to crack.

(6) To lower the melting point of the readily melted constituents, such as potassium and sodium nitrate.

(7) To act as a stirring agent or possibly fining agent and thus assist the melting operation.

Of these seven possible effects, 2, 3, 4 and 5 would undoubtedly be classed as detrimental; 1, however, need not be disadvantageous and within certain limits might be beneficial, whilst 6 and 7 would be classed as advantageous.

The relative effect of these different factors cannot readily be set down. It may be that the advantages of dry batch have been too readily assumed without giving sufficient weight to possible benefits from the presence of definite amounts of moisture; and whilst at first sight the balance of evidence would appear to be against the presence of moisture, it certainly seemed well, especially in these days when no dogma escapes scrutiny, that the matter should be put to the test.

Type of Batch Used and the Character of the Materials.

The type of batch which has been fully investigated by us is the batch for the production of soda-lime glass. Most of the batches were made simply from soda ash, limespar and sand. Certain others, however, contained both soda ash and saltcake.

In this type of batch we have materials which do not differ from one another very considerably in density, as is the case with lead-oxide containing batches. The possibility of making homogeneous mixtures depends, therefore, mainly on the grain size of the different materials and on the moisture present, and presents a somewhat simpler problem from that of the lead-oxide containing batches.

Bearing in mind the fact that grain size may influence the homogeneity of mixing, we have carried out two series of investigations. In Part I. materials were used of grain size approximating to general commercial conditions. In Part II. experiments were made in which the raw materials, particularly the calcium carbonate and soda ash, were sifted so that the grain sizes fell within narrower limits than is the case usually with commercial materials.

For the tests described in Part I., the sand used, namely, Fontainebleau, had a grain size lying between 30 and 100 mesh as measured by the I.M.M. sieves, the coarse and fine material being removed.

The calcium carbonate was in the form of ground limespar and was sufficiently fine to pass, when thoroughly dry, through a 200 mesh sieve. This ground limespar did not cake appreciably with a moisture content up to 4 per cent. Some difficulty was experienced in sieving it, however, since whilst there was no caking into lumps, it did tend to block the holes of a 30 mesh sieve, even when it contained only 1.5 per cent. of moisture.

The soda ash was passed through a 30 mesh sieve before use. About 50 per cent. of this sieved portion was fine enough to pass through a 100 mesh sieve. The caking tendencies of this material are quite well known. When finely ground and kept perfectly dry there is no caking, but when left open to the atmosphere caking readily occurs, and once hardening has set in nothing short of thorough grinding will reduce the material to the form of powder.

Finally, it should be stated that the total amount of batch made up in the experiments was between 40 and 50 lbs., and the same quantity was operated on in all cases.

The Method of Batch Mixing Adopted.

In the whole of the experiments described in this connection the batch was mixed by hand.

In preparing the batch, the materials were weighed out one after the other into a clean enamelled container which was placed on the platform of a weighing machine. With soda lime batches, the sand was weighed out first, and the lime and the soda ash added in order. The ingredients were stirred together roughly and turned out on to a clean, smooth wooden bench, where they were mixed as thoroughly as possible by hand. This operation occupied about 10 minutes. The whole of the batch was then sieved through a ten-mesh sieve into the container again. When the batch was comparatively dry, the batch passed the sieve easily, but if the moisture exceeded 4 per cent., it was invariably necessary to rub down lumps on the sieve before the whole of the material passed through.

The necessity for passing the material through the sieve as well as mixing, if the batch is to be truly homogeneous, is clearly brought out in the results contained in Tables I. and II. These results are the analyses of duplicate samples of batches of the same chemical composition (a), (b), etc., (see Part II.), but of different grain size. In each set an amount of moisture between 3 and 4 per cent. was added, but whereas in Table I. the results are for batches which have been mixed only, those in Table II. are for corresponding batches which have been both mixed and passed through the sieve.

TABLE I.

Batch Mixed but not Sifted.

Batch	H_2O	Insoluble	$CaCO_3$	Na_2CO_3	Total
(a)	4.02	60.91	10.00	25.19	100.12
	4.13	62.33	13.82	20.07	100.35
(b)	3.57	67.76	12.14	15.97	99.44
	3.53	63.90	13.57	19.45	100.45
(c)	3.62	68.46	11.57	16.77	100.42
	3.87	61.07	14.10	20.87	99.91
(d)	3.61	60.53	13.43	22.56	100.13
	4.02	64.67	13.17	17.79	99.65
Calcd.	3.80	61.95	14.13	20.14	100.02

TABLE II.

Batch Mixed and Sifted.

Batch	H_2O	Insoluble	$CaCO_3$	Na_2CO_3	Total
(a)	3.72	61.44	14.96	20.13	100.25
	3.92	61.78	14.40	20.08	100.18
(b)	3.47	62.32	16.36	17.81	99.96
	3.53	62.18	14.25	19.57	99.53
(c)	3.80	61.85	14.62	19.89	100.16
	3.79	62.06	14.70	19.95	100.50
(d)	3.74	61.62	14.44	20.19	99.99
	3.85	62.05	14.05	19.51	99.46
Calcd.	3.80	61.95	14.13	20.14	100.02

It will be seen that the amount of any one constituent is quite distinctly different in the two samples if the batch is not sifted as well as mixed. After sifting, the agreement in composition between any two samples of the same batch is usually very good,

After the whole of the batch had been sieved it was turned out again upon the bench and thoroughly mixed by hand for a second time. Following this it was transferred to the container, covered with a close-fitting lid, and taken to the furnace.

The Methods of Adding Moisture and the Danger of Wet Sand.

The sand used in all batches was dried before use and did not contain an amount of moisture exceeding 0.1 per cent. The limespar moisture content in the first set of experiments was below 1 per cent. During its removal to other premises it became damper, but the moisture content remained very constant at about 3.8 per cent., whilst that of the soda ash varied between 2.5 and 3.5 per cent. When dried batches were to be made up and tested, the raw materials were put through a drying process lasting two or three days.

Moisture was added in one of two ways, either (a) to the sand, or (b) to the batch itself after it had been mixed for the first time. The amount of water to be added was determined after the amount of moisture in the raw materials themselves had been ascertained.

According to the first method, the exact amount of water was added to the sand, which was in turn mixed with the other materials. The requisite weight of sand was spread out in a thin layer on the mixing table and the water sprinkled over it as uniformly as possible. After turning over the sand with an enamelled scoop until it appeared uniformly moist, it was mixed with the other materials in the usual way.

In the second method the mixed batch, before being sieved, was spread out on the table and the water distributed over it uniformly.

In both cases the batches were sieved and mixed, after the addition of water, as indicated previously.

Whilst no difference whatever was noticed either in the homogeneity of the batches or on the rate of melting and fining, between batches mixed by the two methods, provided they were sieved as well as mixed, a distinct difference was obtained when they were not sieved.

When the moist sand in the first method was mixed with the limespar and soda ash, lumps were formed. These lumps invariably consisted of sand grains surrounded by limespar and soda ash. In the second method, when "balling" occurred, the nucleus appeared to be of soda-ash, due presumably to chemical action (hydration) between the soda-ash and water; just as when powdered anhydrous sodium carbonate (soda ash) is thrown into a vessel of water, it forms lumps at the bottom of the vessel and thereafter dissolves but slowly.

Whenever we have melted batches which have not been sieved (and this was done in one or two cases) the rate of melting was less and refining was perhaps rather slower; but, still more important, from the point of view of batch mixing, whenever any sign of stony metal occurred it was always with those batches in which the water had been added to the sand. It was never found when the moisture was added to the batch, unless the moisture content was excessive, say over 10 per cent., in which case balling occurred even after passage through the sieve.

It is quite evident from this that in all ordinary cases (that is, with batches containing not more than 6 per cent. of moisture) damp sand is the real source of danger in producing stony metal. Sieving, however, is a very sound cure for the evil, the lumps being broken down by rubbing through the mesh of the sieve.

Sampling and Testing.

From each of the batches after mixing, two small samples were taken and tested. The amount of the sample was just sufficient for a chemical analysis and amounted to between 5 and 10 gms.

Each sample was analysed in order to determine the amount of moisture present, the sand, the calcium carbonate and the sodium carbonate. The method adopted was to make first an aqueous extract for the sodium carbonate* and to treat the residue with hydrochloric acid. The insoluble portion consisted of the sand together with the very small amount of insoluble matter derived from the soda ash and the limespar. As the ordinary soda ash used contained only 0.06 per cent. of insoluble matter, the light ash *nil*, and the granulated only a trace; and, as further, the limespar contained but 0.22 per cent. of insoluble matter, the figure described as " Insoluble " in the tables below is practically sand.

The moisture was determined by drying a portion at 110-140°. Hydrated sodium carbonate, which is always formed on the addition of water, loses all water of crystallisation at 100°.

PART I. *Batch Materials Composed of a Variety of Sizes.*

Batches Containing Less than 1 per cent. of Moisture. Segregation in Dry Batches.

The materials, when comparatively dry, that is, when they contained less than 1.0 per cent. of moisture, were found to mix together very easily; but unless the particles of the various materials were of the same size (and possibly shape) vibration after mixing caused separation. With 1 per cent. of moisture present the grain size of the materials was found to have a much greater influence upon the thoroughness of mixing than the moisture. In one particular case it was the sand which tended to fall to the bottom of the container when the mixed materials were dry. Consequently, whilst test samples taken from different parts of a dry batch immediately after mixing, agreed very closely in composition,

* Under the conditions of experiment, the sand did not lose any weighable amount through contact with hot aqueous sodium carbonate solution.

standing for some time in the container, especially when subjected to vibration, was accompanied by segregation. Thus, after standing in the neighbourhood of a vibrating machine for an hour, the average silica content of the bottom half of the batch in the container was some one to two per cent. higher than that in the upper half.

Actual figures obtained from samples of batch No. 527b are given in Table III.

TABLE III.

No.	Location.	Percentage Insoluble.
1.	Top of batch	78.15
2.	Top of batch	78.32
3.	Middle of batch	79.05
4.	Middle of batch	79.36
5.	Bottom of batch	80.10
6.	Bottom of batch	79.82
7.	Calculated for batch as a whole	78.70

This segregation is already known to some manufacturers who have used a storage cylinder suspended over the doghouse of a tank furnace. If the arrangement for charging the hopper permits the dry batch to fall some distance vertically into the cylinder, segregation is found to occur, the bottom layers being richer in sand.

On the whole, therefore, dry batches have risk attending their mixing and use.

Batches Containing 1—2 *per cent. of Moisture.*

When the moisture content of the batch varied between one and two per cent., the mixing was readily carried out and the segregation of the materials of the batch was not noticeable on testing. Batch No. 527c was mixed in the ordinary way and a sample taken by removing small portions from all parts of the batch. After standing some time, three samples were taken from different parts of the container,

one from the upper portion, a second from the middle portion, and a third from near the bottom. The insoluble contents of these samples were determined as before and the results are given in Table IV.

TABLE IV.

No.	Location of Sample.	Percentage Insoluble.
1.	Average before standing	78.74
2.	Upper portion after standing	78.70
3.	Middle portion after standing	78.60
4.	Bottom portion after standing	78.88
5.	Calculated for the batch as a whole	78.65

These figures give no indication whatever of any segregation of the batch materials on standing.

Batches Containing 4 per cent. or more of Moisture.

The presence of 4 per cent. of moisture in the batch was found to affect mixing adversely. The phenomena observed, however, differed somewhat according to which of the materials supplied the moisture. If the moisture was added almost entirely through the medium of the sand, the soda ash did not tend to form lumps nearly so readily as when the limespar contained a fair proportion of moisture. In the latter case the particles of soda ash readily caked with the limespar, forming pellets of varying size. Grinding the materials together, apart from any disadvantages which might arise due to the production of much fine material, would not necessarily be of benefit, since caking would readily occur during the grinding process due to the pressure applied to the materials.

PART II. *Batches Made with Materials of Varying Grain Size.*

It seemed to us from the foregoing results that there was quite a definite advantage when mixing batch to have

a small amount of water present; but before attempting to draw definite conclusions as to the most suitable quantity to be added, it appeared wise to ascertain whether, and to what extent, the correct amount varied with the grain size. For it is well known that the absorbent power for moisture varies with the fineness of subdivision of the particles.

Now in practice, the grain size of the materials varies considerably. In the case of limestone, chippings of $\frac{1}{4}''$ to $\frac{1}{8}''$ are frequently employed. It has been pointed out by Dickenson, Dimbleby, Norton and Turner* that the presence of chippings scarcely permit of a thoroughly homogeneous batch being prepared and that granular limestone or limespar is desirable. In the experiments now to be described, and especially as our subsequent melting operations were to be made in pots, we excluded the use of limestone chippings.

In the case of soda ash, three distinct varieties are available for use, namely, the light, the dense and the granulated, the last-named of fairly recent introduction. Granulated forms of limespar may also be had, and by the process of sifting we prepared quantities of this substance with grains between 30 and 80 mesh and also finer than 80 mesh. Using these specially prepared materials as well as the normal materials mentioned in Part I., we made up sets of batches as follows:—

(a)	sand	30—100	mesh,	soda	ash	30—100	mesh,	Limespar	30—200
(b)	,,	30—100	,,	,,		light†	,,	,,	30—200
(c)	,,	30—100	,,	,,		30—100	,,	,,	80
(d)	,,	30—100	,,	,,		30—100	,,	,,	30—80
(e)	,,	30—100	,,	,,		granulated‡	,,	,,	30—80

Generally speaking, although some of these batches had particles of all three materials very much of a size, they

* J. Soc. Glass Tech., 1922, **6** 234.

† 98 per cent. of the light ash passed through the 30 mesh sieve; 17 per cent. passed through the 70. The material contained 1.26 per cent. of moisture.

‡ 84 per cent. passed through the 30 mesh sieve, 28 per cent. through the 70. 1.46 per cent. of moisture was present.

still lacked homogeneity when mixed without passing through a sieve. The advantage of passing through the sieve has already been demonstrated. The figures in all the following tables are for mixed and sieved batches.

The results found when different amounts of water were added may now briefly be stated, together with the results of the analysis of duplicate samples from each batch.

Batches Containing 2—3 per cent. of Moisture.

Table V. contains the results of the tests on the composition of the duplicate samples taken. From these results it would appear that the least homogeneous batch was that containing granulated soda ash and granulated limespar (30-80), a result scarcely expected, as the particles of the three materials are so similar in size. From the point of view of ultimate homogeneity, there was little to choose between the other four batches.

In regard to the general behaviour during mixing, batch containing fine limespar (batch a) had a tendency to cling together, although there was no caking. When light soda ash was present (batch b), there was a slight tendency to balling, but no serious difficulty and no caking. With limespar in grains of 30-80 mesh the clinging effect as mentioned in (a) disappeared.

TABLE V.

Batch	H_2O	Insoluble	$CaCO_3$	Na_2CO_3	Total
(a)	2.55	62.58	14.96	20.03	100.12
	2.60	62.85	14.76	19.95	100.16
(b)	2.52	62.98	14.68	19.69	99.87
	2.55	62.78	15.62	19.63	100.58
(c)	2.80	62.95	13.98	20.04	99.77
	2.80	62.52	14.81	20.25	100.38
(d)	2.63	61.60	15.34	20.43	100.00
	2.60	61.89	15.61	20.03	100.13
(e)	2.78	63.16	14.18	19.95	100.07
	2.65	61.41	16.15	19.83	100.04
Calcd.	2.65	62.69	14.29	20.37	100.00

Batches with 3—4 per cent. of Moisture.

From the analytical results recorded in Table VI., only the batch containing light soda ash and finely ground limespar showed any departure from homogeneity. Between the others there is little to choose.

All of the batches prior to sieving had a tendency to lumpiness or caking, the effect being very noticeable in the batch containing light soda ash. Also, before sifting, the batch with the limespar of grain size 30-80 mesh became distinctly "balled," the larger grains of limespar apparently acting as nuclei. These points are of importance when mixing by machine, since passage through a sieve after mixing is not adopted.

TABLE VI.

Batch Mixed and Sifted.

Batch	H_2O	Insoluble	$CaCO_3$	Na_2CO_3	Total
(a)	3.72	61.44	14.96	20.13	100.25
	3.92	61.78	14.40	20.08	100.18
(b)	3.47	62.32	16.36	17.81	99.96
	3.53	62.18	14.25	19.57	99.53
(c)	3.80	61.85	14.62	19.89	100.16
	3.79	62.06	14.70	19.95	100.50
(d)	3.74	61.62	14.44	20.19	99.99
	3.85	62.05	14.05	19.51	99.46
Calcd.	3.80	61.95	14.13	20.14	100.02

Batches with 4—5 per cent. of Moisture.

The ordinary batch (a) was markedly lumpy, but did not cake extensively. With light ash the lumpiness was more pronounced both before and after sifting and there was a tendency to caking. Fine limespar caused the production of a distinctly lumpy batch even after sifting and there was again a slight caking. This batch was the first of the series to feel at all damp to the touch. The coarser limespar, 30-80 mesh, gave a batch which was no more lumpy than when only 3 to 4 per cent. of moisture was present. The batch caked slightly, however, and was damp to the touch.

The granulated soda ash batch was only very slightly lumpy and hardly became caked at all, even under pressure.

So far as homogeneity is concerned, all the final batches were satisfactory in composition, as is indicated in Table VII.

TABLE VII.

Batch	H_2O	Insoluble	$CaCO_3$	Na_2CO_3	Total
(a)	4.67	61.08	14.61	19.95	100.31
	4.68	60.95	13.86	20.43	99.92
(b)	4.12	61.36	14.36	19.95	99.79
	4.16	61.74	14.48	19.79	100.17
(c)	4.74	61.70	14.09	19.29	99.82
	4.67	61.73	14.35	19.51	100.26
(d)	4.04	61.11	16.30	18.97	100.42
	4.07	60.83	16.43	19.15	100.48
(e)	4.34	60.60	15.75	19.11	99.80
	4.36	61.08	15.28	18.95	99.67
Calcd.	4.45	61.53	14.03	20.00	100.01

Batches Containing 6 to 7 per cent. of Moisture.

The batch containing the ordinary grades of material was very lumpy, caked slightly, but did not feel at all damp. That made up with the light ash gave a batch similarly lumpy, but it also caked in a pronounced fashion under pressure and felt slightly damp. Whilst considerable lumpiness was evident in the fine limespar batch, even after sifting, the caking was only slight.

The 30-80 mesh limespar gave a batch in which the lumpiness and balling were more noticeable and caking quite distinct under pressure. This was the first of the 30-80 mesh limespar batches not only to feel damp, but also to have a damp appearance. In general, the 30-80 mesh limespar batches mixed better than the fine limespar batches, or at any rate appeared to do so. Thus the 2 to 3 and 3 to 4 per cent. moisture batches were not unlike ordinary batches, whilst the 4 to 5 per cent. moisture batch just tended to cling together like an ordinary batch with only 2 to 3 per cent. of moisture.

The granulated soda ash showed slight lumpiness and caking under pressure and also felt slightly damp.

Table VIII. contains the composition of the duplicate samples of each batch. These results quite evidently show that the degree of mixing is inferior in comparison with the batches containing smaller amounts of moisture, and we have no hesitation in condemning the use of 6 to 7 per cent. of water.

TABLE VIII.

Batches with 6 to 7 per cent. of Moisture.

Batch	H_2O	Insoluble	$CaCO_3$	Na_2CO_3	Total
(a)	6.63	59.91	14.10	19.11	99.75
	6.33	60.50	14.57	18.97	100.37
(b)	6.78	59.50	13.81	19.79	99.88
	6.47	60.34	13.96	19.66	100.43
(c)	5.94	61.25	13.57	19.32	100.08
	7.33	56.58	15.62	20.91	100.44
(d)	6.19	58.74	15.91	19.57	100.41
	6.04	59.94	15.22	18.97	100.17
(e)	6.53	59.46	14.02	19.89	99.90
	6.11	58.06	16.10	20.23	100.50
Calcd.	6.40	60.29	13.74	19.59	100.02

General Conclusions.

In deciding on the advantages or disadvantages of the presence of moisture in a batch, we have to bear in mind that other factors are concerned than the mixing, and a full decision must not be taken until the study of the effect of moisture on the melting and working of the glass has been made. That study is reserved for a further paper.

For the moment, therefore, we have to confine ourselves to the subject of the influence, beneficial or otherwise, of moisture on batch mixing. In arriving at a decision here there are three factors to be taken into account, namely, the

homogeneity of the batch as tested by the analysis of different portions, the length of time taken to obtain homogeneity, and thirdly, general difficulties, such as the balling up or lumpiness of the batch observed during the operation or when the batch was standing.

In regard to the thoroughness of mixing, most of the batches we prepared would probably be more homogeneous than the average batch prepared in a works even equipped with a machine. The biggest variations, taking the batches as a whole, were found when the moisture content was 6 to 7 per cent., and we have already stated we have no hesitation in condemning so much moisture as unsuitable and detrimental to the mixing.

At the other end of the scale we have shown that not only very dry batches, but all batches containing up to 1 per cent. of moisture, although they are readily mixed, are also fairly readily, so to speak, unmixed; that is to say, segregation tends to occur. This means that the presence of moisture is desirable to preserve homogeneity.

In regard to the other ranges of moisture content tested, a decision is less easy to make on the basis of the analyses. We have attempted by an analysis of the chemical tests to decide between them, and have arrived at the conclusion that, generally speaking the best mixing from the point of view of composition was obtained when 3 to 4 per cent. of moisture was present. The results in this case appear to be somewhat better than those when either 2 to 3 or 4 to 5 per cent. was added.

The time taken to prepare a homogeneous batch is the second factor which may help to decide on the amount of moisture and the size of the grain particles to be used. Homogeneous batches could generally speaking be obtained even when much moisture was present and when the particles varied considerably in size, provided they were not larger than 20 to 30 mesh. Whilst this was the case, however, practical considerations would necessarily put into dis-

favour any particular batch which required an unduly long mixing.

In our experiments we have pointed out that two mixings were given, one before and another after the sifting process. Each of these operations took 10 minutes, these times being standard times. Any difference, therefore, between the total length of time necessary to prepare the batch was due to differences in the time required to pass the batch through the sieve. Generally speaking, we found the time needed for sifting increased with the amount of moisture present; thus, with 3 per cent. the time for sifting was approximately 5 minutes, but with 7 per cent., 10 minutes were needed.

It was found that when the limespar was very fine and when this fine limespar was wet, that the pellets formed with the soda ash were distinctly hard, and 50 per cent. longer time was needed to break these up and get them passed through the sieve than when coarser limespar was employed or when the water was added either through the agency of the sand or through the batch as a whole.

The difference in the total time needed for mixing was only a matter of about 5 minutes and perhaps it does not seem very great. Nevertheless, there is a distinct difference and one which is in favour of the moisture content not exceeding about 3—4 per cent.

Of the influence of grain size it is only possible to speak in general terms, since the effects observed here come out partly in the analysis and partly in the general phenomena such as caking and balling. Thus, the batches with light soda ash, as also those with very fine limespar, do not give such homogeneous batches as those containing the ordinary materials (that is, ordinary sand, ordinary soda ash and limespar from 30 mesh upwards). On the other hand, the batches prepared with granulated soda ash and granulated limespar (30 to 80 mesh) are less satisfactory from the point of view of composition, although from the ease with which

the batches were observed to be mixed during the actual mixing operation the granulated limespar batches appeared to be superior to those containing the fine limespar.

We have already indicated the three fairly definite conditions under which balling or agglomerating occurs when moisture is present, namely, that in which the sand acts as a nucleus, secondly, in which the soda ash itself cakes, and thirdly, in which the limespar and soda ash cling together in pellets, this last-named occurring when the limespar is wet. The caking of the soda ash was, generally speaking, only at all prominent when the light ash was employed, and for this reason again the light ash is scarcely to be recommended.

On the whole it appears to us that a certain amount of moisture is desirable in batch mixing. The most suitable amount, judging by all the tests applied, appears to be in the neighbourhood of 3 per cent., whilst it should not exceed 4 per cent. Moreover, in using such batches, the best results will be obtained when light soda ash and very finely ground limespar are excluded. Further, if, in order that a batch may contain a given amount of moisture, it is necessary to add water, the latter should be added to the batch as a whole and not to the sand, the limespar or the soda ash singly.

In all these observations, as already indicated, hand mixing has been carried out. It would be well if some additional experiments could be made in a machine. The general principles already set out in this paper may with reason be expected to apply to the machine also. There is, however, in the machine, nothing quite comparable to the use of a sieve through which the batch was forced in the experiments here described. It may be that the knives in the case of a machine with a stationary body, or the projections from the walls of the drum in the case of the machine with a rotating body, may break up agglomerations in the manner somewhat similar to the 10 mesh sieve. It would be well, however, that a few experiments on this point should be carried out.

Tests with Other Batches.

In addition to the particular batch on which all the foregoing tests were carried out, four others, as set out in Table IX., were also tested.

TABLE IX.

Batch	528	529	519a	519b
Sand	1000	1000	1000	1000
Soda ash	296	270	556	556
Saltcake	71	104	—	—
Limespar	240	240	—	—
Alumina (hydrated)	—	—	89	—
Alumina (calcined)	—	—	—	58
Coke	5	7	—	—

The general results obtained tally closely with those got from the systematic study of the sand, soda ash, limespar batches, and we may conclude, generally speaking, that moisture is an advantage in the mixing with these batches, and further, the most effective amount, generally speaking, is between 3 and 4 per cent. It should not, however, exceed this amount.

In regard to the lead-oxide containing batches, it has not been possible to carry out a series of systematic tests. Some batches, however, were prepared during the tests on the effect of chlorides and sulphates on the properties of potash-lead-oxide glasses.

We found in these that the dry batch itself contained approximately 2 per cent. of moisture. When the batch was made it was observed that each movement of the batch brought about a distinct separation of the particles. Moreover, on standing with vibration, separation began to occur, the sand and the red lead tending to accumulate in the lower portions. It must be borne in mind that with a batch of this kind we also have the additional factor of the greater density of the lead-oxide to deal with as compared with the other materials.

With batches containing 4 per cent. of moisture the separation of the particles was completely prevented. No dustiness was experienced, and although in the early stages of mixing there was a tendency to form balls or lumps, these were broken up as the mixing proceeded and the batch ultimately obtained was in a condition much superior to that which contained only 2 per cent. of moisture.

20th October, 1922.

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CONFIDENTIAL TO
THE MEMBERS OF
THE GLASS
RESEARCH
ASSOCIATION.

LONDON
GLASS RESEARCH ASSOCIATION,
50, Bedford Square, W.C. 1.

NOTE.

The Council of the Association does not hold itself responsible for the opinions expressed by the contributors of the various articles.

Contents.

I. The Function of Arsenic in Glass.

A Report by the Department of Glass Technology, University of Sheffield, on Investigations carried out on behalf of the Glass Research Association.

Programme of Research, 1922.
Item 7 (c).

Abstract: The function of arsenious oxide on the melting of soda-lime glasses has been tested by meltings carried out in covered pots at a temperature of 1400° C. Contrary to general belief, the arsenious oxide added to the batch is not expelled during the melting process. Practically the whole of it is retained when the amount added is about one to two parts per 1000 parts of sand; whilst 60 per cent. or more is retained even when 250 parts per 1000 are added. In batches containing neither oxidising nor reducing agent, part of the arsenious oxide, from 40 to 70 per cent., is converted to arsenic oxide and is found in this condition in the glass.

No beneficial action has been found in the experiments to be exerted by arsenious oxide either on the rate of melting or on the refining of the glass. The presence of arsenious oxide in amounts greater than 2 parts per 1000 of sand is liable to lead to the formation of a scum of high silica content and when present in amounts from 150 to 250 parts per 1000, opacity in varying degrees is produced.

The presence of arsenious oxide does definitely reduce the green tint in glass due to iron oxide and may therefore be regarded as a decolouriser.

THE request of the Association was that following up the study of the effect of moisture on the melting of glass batches, the influence of arsenic when added to these same batches should be tested.

It seemed to us that before this particular investigation could intelligently be carried out it was essential that the effect of arsenious oxide when added to normally dry batches should be thoroughly understood. For this reason the report now presented is confined to a statement of the

results obtained when glasses are melted from batch containing less than 2 per cent. of moisture; that is to say, batches which in normal factory practice would be regarded as dry.

How far back in glassmaking practice the addition of white arsenic occurs we have not yet been able to trace. It was certainly in use early in the 19th century, the volume on "Porcelain and Glass" in Lardner's Cabinet published in 1832,[1] referring to it as being used to correct the excessive use of manganese, whilst it was also a powerful flux, was useful both in removing carbonaceous matter, and also in stirring the glass. The reference in question stated that there was a great temptation to its use for the purposes mentioned because of its cheapness, but that if improperly incorporated with the other ingredients of the glass the latter appeared cloudy or milky, a fault which increased with the lapse of time, whilst the presence of arsenic also assisted in the gradual decomposition of glass.

What truth there is in the view that arsenious oxide reduces the durability of the glass the writer cannot say, but the other functions of arsenic mentioned are those which it is still commonly regarded as fulfilling.

There appears also to have been the view extant (although it does not appear general) that arsenic might also serve as a colouring agent, since Gillinder[2] states: "In many flint receipts it is used as colouring matter; for my part I consider that this is not of the slightest use whatever in flint glass, in fact it is an injury."

Some fifty years later Tscheuschner[3] stated that the addition of arsenious oxide to the batch did not lead to the addition of arsenic to the glass,[4] since it was readily volatile,

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[1] "Treatise on the Origin, Progressive Improvement and Present State of the Manufacture of Porcelain and Glass," Longmans, 1832.

[2] Treatise on Glass Making, 1854, page 23.

[3] Die Glasfabrikation, Dresden, 1885, page 23.

[4] Tscheuschner makes the rather curious statement that if it did (that is to say, if the arsenic did enter the glass) the glass would alter in the air and become iridescent.

being almost completely removed and only found in the glass in very rare cases. He refers to Baedeker as having found only 0.022 per cent. of arsenious oxide in a coloured glass.

According to Tscheuschner the action of arsenious oxide in glass melting was partly mechanical, due to its volatility, the bubbles stirring up the glass, and partly chemical. In its chemical action arsenious oxide might act as an oxidising agent, becoming reduced to elementary arsenic, and in consequence being expelled in any case because of the volatility of this element. It also served to remove the colour due to the excessive addition of manganese dioxide.

Henrivaux [5] considered that arsenious oxide assisted in the fusion of glass, but it was preferable to employ for this purpose sodium arsenate.

Coming down to modern times, Dralle [6] in 1911 expressed almost precisely the same views [7] as Tscheuschner in 1885, merely adding one additional statement, namely, that arsenious oxide was useful in reducing the excess colour due to small overdoses of selenium as well as of manganese dioxide.

The orthodox views in regard to the function and usefulness of arsenic appear to have first been challenged in America, and since 1910 the really valuable contributions to the subject have come from that country.

In 1910 Mr. Takahashi, during the course of a discussion,[8] expressed the view that both antimony and arsenious oxides were not necessary ingredients of the batch, whilst Silverman stated " The claim is made that arsenic and antimony increase gloss and hardness and prevent the reduction of lead. I do not believe it." He also instanced the

5 Le Verre et le Crystal, 1897; pages 397, 398.

6 Die Glasfabrikation, 1911, Vol. I., page 186.

7 Despite the fact that W. Fresenius (Zeitsch. analyt. Chem., 22, 397) directed attention to the appreciable amounts of arsenic retained in glass, particular reference being made to samples of Bohemian and of Thuringian glass, which had been found to contain 0.2 and 0.08 per cent. respectively of elementary arsenic.

8 " The Chemist and the Glass Manufacturer," A. Silverman, Trans. Amer. Cer. Soc., 1910, 12, 186.

case of cloudy glass being obtained from a flint glass containing arsenic and antimony, a clear glass with a highly polished surface resulting when these oxides were omitted.

C. J. Brockbank,[9] in discussing the technical control of a window tank furnace, said, in regard to arsenious oxide, that it is doubtful if it has any beneficial action.

The first glass technologist who appears to have shown that arsenious oxide was not expelled from the glass on melting, but most of it retained, was S. R. Scholes,[10] who showed that both in a soda-baryta and also in a lead-potash glass the greater part of the arsenious oxide added was retained in the glass, almost all in the quinquevalent state. Within a short time of the publication of this paper F. Gelstharp,[11] working along other lines, showed that in the case of a sample of plate glass which he analysed, 56 per cent. of the original arsenious oxide was left in the glass, all being present as As_2O_5 and none as As_2O_3, despite the fact that the glass melting proceeded under reducing conditions. He also found that only about one quarter of the arsenious oxide was lost when 100 grams of Na_2CO_3 and 5 grams of As_2O_3 were slowly heated to 900° C. in an open crucible, whilst with 100 grams of calcium carbonate instead of the sodium carbonate, the loss was a little more than a third when the temperature was raised slowly to 1090° C.

These experimental results clearly indicated that the old view that arsenious oxide was wholly expelled during the process of glassmaking was quite in error.[12] The later work by E. T. Allen and E. G. Zies [13] gave additional support to the view that arsenious oxide was retained in glass to a very great extent. It may be remarked, however, that in four of the five glasses examined by these investigators, nitre had been added to the batch.

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[9] Trans. Amer. Cer. Soc., 1915, **17**, 222.

[10] Trans. Amer. Cer. Soc., 1913, **15**, 585.

[11] J. Ind. Eng. Chem., 1912, **4**, 16.

[12] Unless a considerable proportion of carbonaceous matter was present.

[13] J. Amer. Cer. Soc., 1918, **1**, 787.

To sum up, it would appear that arsenious oxide is not all expelled during the process of glassmaking, and that a considerable proportion of it may be converted to arsenic oxide. In such case it can scarcely be of very great value as a refining agent when added to the batch at the outset, whatever may be the action when a lump is added towards the end of the founding operation. Indeed, it will be seen that several observers have questioned the utility of arsenious oxide at all as a batch constituent. Distinct disadvantages, in fact, have been found to accompany its use; first, its liability under certain conditions to produce milkiness; secondly, the tendency to make the colour of window glass unstable in sunlight,[14] and thirdly the discolouring action produced during lampworking when small amounts of it are present in glass tubing.[15]

More readily recognisable advantages are its function in counterbalancing excess of selenium or manganese dioxide and its scavenging action in removing carbonaceous matter, although it would be an expensive method of carrying out the latter operation if this were its only function. It has also been stated to increase the crushing strength of glass,[16] whilst it is not infrequently referred to as possessing a decolourising action of its own.

To have investigated all the points raised above, a lengthy investigation would have been necessary, but it did appear desirable, before complicating the issue with the effect of moisture, to ascertain quite definitely—

(1) Whether or not arsenious oxide was retained during the melting of a non-oxidising batch, and if so, in what form and to what extent.

(2) Whether or not arsenious oxide assisted in the melting operation, and if so what was the maximum amount which should be used.

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[14] C. J. Brockbank, loc. cit.
[15] F. W. Hodkin and W. E. S. Turner, J. Soc. Glass Tech., 1919, **3**, 158.
[16] R. L. Frink, Trans. Amer. Cer. Soc., 1909, **11**, 313.

(3) Whether or not arsenious oxide assisted in the refining process.

(4) Whether or not arsenious oxide acted as a decolouriser.

THE GLASSES TESTED.

The batch composition used throughout the experiments was the soda-lime batch previously used by us in the investigations on the influence of moisture, namely :—

Sand	1000
Soda ash	325
Limespar	228

The batch was a moderately dry one and contained in all cases between 1.6 and 1.7 per cent. of moisture.

To the above batch, arsenious oxide was added in amount bearing a definite ratio to the sand. The particulars are stated in Table I.

TABLE I.

No. of Glass.	Parts of Arsenic per 1000 of Sand.	Approx. percentage of Arsenic (As_2O_3) in the Glass.	Pot Size.
527M	1	0.10	56 lb.
527P	2	0.15	56 ,,
527P/2			100 ,,
527/3			100 ,,
527N/2	3	0.20	100 lb.
527N/3			100 ,,
527N/4			56 ,,
5270	4.5	0.30	56 lb.
5270/2			100 ,,
5270/3			100 ,,
527Q	7.5	0.50	56 lb.
527Q/3			100 ,,
527R	10.	0.75	56 lb.
527R/2			100 ,,

The meltings were carried out at 1400° C. in pots of two different sizes, namely, a 56-lb. pot and a 100-lb. pot, both being of the covered type.

During the charging in of the batch fumes were evolved, but only during the actual charging operation so that the obvious loss of arsenious oxide occurred during a very brief interval of time only.

Observations were made from time to time of the rate at which the batch melted and at which seed was removed, and finally, samples of the glass were worked out, being cast into discs and drawn into tubing. Samples of the glasses were analysed.

The Retention of Arsenic by Soda-Lime Glasses.

The various samples of glass melted were analysed completely, including the determination of both the arsenious oxide and arsenic oxide present; the method employed in the last-named operation was that described by Allen and Zies,[17] and was tested by us beforehand and found to work well.

The results of the analysis are set out in Table II.

The analyses furnish a very definite and complete answer to the question as to whether or not arsenious oxide in a soda-lime batch is retained in the glass. It will be seen, indeed, when the column is examined which states the total arsenic present, calculated as As_2O_3, that almost the whole of that oxide added to the batch was retained. At any rate, this is true up to about 5 parts of arsenious oxide per 1000 of sand, and we must infer that the amount lost by volatilisation during the process of charging in the batch was very small, certainly with the proportions of arsenic named.

The next point which is clearly brought out is that despite the absence of an oxidising agent in the batch a considerable proportion of the arsenious oxide is converted to the arsenic condition. The actual proportion under the conditions of experiment appears to have been about one-half. It varied somewhat with the batch, the proportion (see Table III.) falling as the amount of arsenious oxide per 1000 of sand increased from 1 to about 5 parts per 1000. In the other glasses, however, there is no continuation of this fall.

[17] Loc. cit.

TABLE II.

No.	SiO_2	As_2O_3	As_2O_5	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	Total	Total As as As_2O_3
527M	75.85	0.03	0.05	0.27	0.06	9.56	trace	14.26	100.08	0.07
Calc.(M)	75.70	(0.08)	—	0.14	0.03	9.60	0.05	14.40	100.00	0.08
527P	75.00	0.08	0.10	0.28	0.06	9.31	trace	14.96	99.79	0.17
527P/2	75.40	0.07	0.10	0.32	0.04	9.54	,,	14.50	99.97	0.16
527P/3	75.80	0.08	0.07	0.17	0.05	9.68	,,	13.90	99.75	0.14
Calc.(P)	75.65	(0.15)	—	0.14	0.03	9.59	0.05	14.39	100.00	0.15
527N/2	75.26	0.11	0.10	0.21	0.05	9.74	trace	14.23	99.70	0.20
627N/3	75.66	0.12	0.08	0.13	0.05	9.70	,,	14.42	100.16	0.19
627N/4	75.46	0.11	0.11	0.16	0.05	9.81	,,	14.04	99.74	0.20
Calc.(N)	75.60	(0.23)	—	0.14	0.03	9.58	0.05	14.37	100.00	0.23
5270	75.06	0.23	0.17	0.41	0.09	9.08	trace	14.94	99.98	0.38
5270/2	75.04	0.23	0.16	0.34	0.06	9.66	,,	14.67	100.16	0.37
5270/3	75.10	0.13	0.21	0.26	0.04	9.92	,,	14.22	99.88	0.31
Calc.(O)	75.51	(0.34)	—	0.14	0.03	9.57	0.05	14.36	100.00	0.34
527Q	75.30	0.15	0.46	0.17	0.05	9.26	trace	14.50	99.89	0.55
527Q/3	74.88	0.29	0.22	0.13	0.05	9.64	,,	14.67	99.88	0.48
Calc.(Q)	75.33	(0.57)	—	0.14	0.03	9.56	0.05	14.32	100.00	0.57
527R	75.60	0.33	0.38	0.24	0.06	9.60	trace	13.76	99.97	0.66
527R/2	74.92	0.36	0.48	0.22	0.05	9.50	,,	14.42	99.95	0.78
Calc.(R)	75.19	(0.75)	—	0.14	0.03	9.54	0.05	14.30	100.00	0.75
Glass with no As.	75.76	—	—	0.14	0.03	9.61	0.05	14.41	100.00	—

TABLE III.

No. of Glass.	Ratio $\frac{As_2O_3 \text{ as } As_2O_5}{\text{Total } As_2O_3}$
527M	0.57
527P	0.53
527P/2	0.56
527P/3	0.43
527N/2	0.45
527N/3	0.37
527N/4	0.45
527O	0.38
527O/2	0.38
527O/3	0.58
527Q	0.73
527Q/3	0.35
527R	0.50
527R/2	0.63

It is of interest to quote the results of determinations by Allen and Zies, of the arsenic contents of several glasses. These results are quoted in Table IV.

TABLE IV.

Type of Glass.	As_2O_3 by Calcn.	As_2O_5	As_2O_3	Total as As_2O_3	Percent. Loss of As_2O_3
Flint, PbO = 42 %...	0.48	0.38	0.05	0.38	21
Flint, PbO = 38 %...	0.40	0.35	0.05	0.35	12
Ba Flint— PbO = 38 % ... BaO = 6 % ...	0.26	0.23	0.03	0.23	11
Spectacle crown ...	1.09	0.99	0.08	0.93	15
Green plate	0.36	0.18	0.09	0.24	33

It will be observed that there was in all cases some loss of arsenious oxide, the loss being least from the first four glasses which were made from batches containing nitre. In these four glasses, also, practically all of the arsenic retained was in the arsenic condition. One would naturally expect this greater proportion of arsenic oxide in the batches containing oxidising material. In the green plate glass 66 per cent. of the arsenic was present as arsenic oxide, a figure somewhat more in agreement with our own results, although rather higher.

The Retention of Arsenic when Used in Large Proportions in the Batch.

In all the preceding glasses the maximum amount of arsenious oxide added to the batch would only produce 0.7 per cent. if all was retained in the glass. It seemed to be of interest to proceed beyond this amount and ascertain whether larger proportions of arsenic could be added without great loss being sustained during the melting process.

A number of experiments were therefore carried out in which, to the standard batch, amounts of arsenious oxide of 20, 25, 50, 100, 150, 200 and 250 parts per 1,000 of sand were added.

It did not appear necessary or even desirable that the large scale meltings should be made with such large amounts of arsenious oxide, and it was deemed sufficient in order to obtain comparable results to carry out these meltings in crucibles holding about one pound of glass.

The main series of experiments was carried out at 1,350°, some additional experiments being made later at 1,400°. In all cases the period of melting was 3½ hours.

In each case the furnace gases were cut off at the moment of charging on the batch in order that the escape of arsenical fumes might be noted. In the cases of the batches with 20, and 25 parts per 1,000 of sand, the amount of fume appeared to be negligible, but as the proportion of arsenious oxide increased still further, so also did the density of the fumes, and in the case of the batches with 150, 200 and 250 parts, the whole furnace room smelled of the fume for at least half an hour after charging on and the gas flames were tinted for about an hour.

Samples of the glasses were poured in most cases, but with the batch containing 200 and 250 parts of arsenious oxide a glass was not produced at 1,350°. In these cases the mass left in the crucible was analysed for arsenic.

The results of the analyses are stated in Table V.

TABLE V.

Retention of Arsenic in Glasses melted at 1,350°.

As_2O_3 in batch per 1000 sand.	Observed As_2O_5	Observed As_2O_3	Total As. as As_2O_3	Calculated Total As_2O_3
20	1.27 1.26	0.58 0.57	1.66 1.65	1.50
25	1.58 1.58	0.57 0.52	1.92 1.86	1.86
50	2.58 2.58	1.14 1.04	3.34 3.26	3.65
100	4.18* 4.28	2.41 2.34	6.00 6.01	7.13
150	5.41 5.35	2.92 3.07	7.57 7.68	10.21
200	7.35 7.40	4.75 4.80	10.99 11.17	13.17
250	8.64 8.65	5.04 5.04	12.47 12.48	15.93

* Slight loss during analysis.

At a temperature of 1400°, glasses were produced and poured even with batches containing 200 and 250 parts of arsenious oxide. These glasses were analysed and the results are stated in Table VI.

TABLE VI.

As_2O_3 in batch per 1000 sand.	Observed As_2O_5	Observed As_2O_3	Total As. as As_2O_3	Calculated Total As_2O_3
200	7.91 7.80	4.26 4.22	11.07 10.93	13.17
250	7.23 7.00	4.61 4.83	10.63 10.66	15.93
250	5.58 5.29	3.63 3.87	8.43 8.43	15.93

It will be noted that the two sets of meltings with 250 parts of arsenic in which different amounts of this material were retained. The variation is affected by the extensiveness to which a scum forms on the surface of the glass during melting, the second sample of glass being one in which the scum was pronounced.

It will be seen that in all cases, even with such large amounts of arsenic, the proportion retained is very great.

Moreover, under these conditions of melting, the proportion of arsenic oxide was always greater than arsenious. In the cases of the glasses made from batches containing from 20 to 50 parts, the ratio was more than two to one. All these results go conclusively to prove that arsenious oxide is retained in a very large measure during the melting of glass.

In our own experiments the investigations have been confined to soda-lime glasses. Reference may again be made to the fact, however, that the retention of arsenic was also found in soda baryta glasses by Scholes and in potash-lead glasses by Scholes and by Allen and Zies. Whilst the percentage retained will probably vary with the amount of organic matter present, it appears to have little dependence on the presence of small quantities of oxidising material, the main action of the latter being to increase the proportion of the arsenious oxide converted to the arsenic state.

Seeing that, on the one hand, in a batch containing oxidising material *all* the arsenic is not retained, whilst, on the other, there is no considerable loss from a neutral batch, it would be of interest to determine how far the presence of small amounts of carbonaceous matter influence the volatilisation of arsenic.

The Effect of Arsenious Oxide on the Melting of Soda-Lime Glass.

From the periodic observations made during the melting of the glasses the results summarised in Table V. were obtained.

The most readily melted of all the batches were those containing 2 parts of arsenious oxide per 1000 of sand. It is clear that continued addition of arsenious oxide does not improve the rate of melting. The question that remains is whether or not arsenious oxide is more effective than moisture in its influence on melting. A comparison with the corresponding glasses containing moisture but not arsenic showed that the latter conferred no benefit on the rate of melting.

TABLE V.

No. of Glass.	As_2O_3 per 1000 of sand.	Minutes, between fillings.	Time hours) to obtain batch free.	Remarks.
527M	1	120	4 hours	Required 1½ hours to melt down from the opaque semi-fused condition.
527P	2	90	3 ,,	Almost batch free in 2 hours.
527P/2		90	3 ,,	Ditto, ditto.
527P/3		95	3¼ ,,	Not batch free in 3 hours.
527N/2	3	120	3½ ,,	Not batch free in any case until after 3 hours.
527N/3		120	3½ ,,	
527N/4		120	3½ ,,	
527O	4.5	105	3½ ,,	
527O/2		105	3½ ,,	
527O/3		120	4 ,,	Not batch free at 3½ hours.
527Q	7.5	120	4 ,,	Not batch free at 3½ hours.
527Q/3		120	4 ,,	
527R	10.	120	4 ,,	Not batch free at 3½ hours.
527R/2		140	4 ,,	

In face of the traditional belief in the fluxing power of arsenious oxide, the above results seem to us to deserve a little further examination. We therefore decided to carry out a number of small scale meltings with large amounts of arsenious oxide to ascertain if with considerable quantities present ready melting could be obtained. The result demonstrated very clearly that readier melting was not obtained.

In the first set of such experiments, amounts of 150, 200 and 250 parts per 1000 of sand were used and the temperature of melting was 1350° C. Not one of these mixtures gave a glass that could be poured, and after cooling the specimens and breaking the pots, only that containing 150 parts of arsenious oxide gave anything approaching a clear glass. The two others were porcelain-like and contained large cavities, obviously corresponding to a spongy gas-filled mass.

Some experiments made at 1400° showed that glasses could be obtained from all three batches, and this led us

to a further careful series of experiments carried out at four different temperatures, namely, 1325°, 1350°, 1375° and 1400° C. In this last comparison series the mixture with 150 parts of arsenic was omitted. There was used, however, by way of comparison, the batch containing no arsenic. The following table (Table II.) summarises our experience:—

TABLE II.

Influence of Large Amounts of Arsenious Oxide on the Melting of Soda-Lime Batches.

Melting Temperature.	Amount of As_2O_3 per 1000 of sand. 0.	200.	250.
1325° C.	Melted; somewhat seedy; poured.	Porcelain-like mass; no real fusion.	Porcelain-like and spongy.
1350° C.	Melted; seedy; poured.	Melted & poured; clear glass in quickly chilled portions, opal where cooled more slowly.	Porcelain-like.
1375° C.	Melted; practically seed free.	Melted; less opal and more clear glass than at 1350° C.	Melted; opal and lumpy.
1400° C.	Ditto.	Melted; opalescent only.	Melted; opalescent.

It will be seen that only the batch without arsenious oxide melted at 1325°, whilst that with 250 parts of arsenious oxide required a temperature of 1375°. It is to be remarked that at the higher temperatures of 1375° and 1400°, where molten glasses were actually obtained, those with arsenic present were more fluid than the one without arsenic. In the sense, therefore, in which the term "flux" in glass melting is usually employed, namely, that of causing readier melting, that is, melting at a lower temperature, arsenic must be regarded quite definitely as not a flux, when used in conjunction with soda-lime batches.

One phenomenon of very considerable practical interest appeared during the melting operation with certain glasses melted in the 100 lb. pots. The phenomenon did not occur with 56 lb. pots. With the batches containing 2, 3, 4, 5, and 7.5 parts of arsenious oxide per 1000, a thick, hard,

porcelain-like crust appeared on the surface of the glass. A portion of this scum, removed from glass No. 527P/3, had the following composition:—

SiO_2	86.00
As_2O_3	0.06
As_2O_5	0.03
Al_2O_3	0.24
Fe_2O_3	0.04
CaO	4.82
MgO	trace
Na_2O	8.92

The glass 527R had no scum on the surface, but the scum was observed to occur on the small meltings in which amounts of arsenious oxide from 20 up to 250 parts per 1000 of sand were present.

This scum will be seen to have a very high silica content and was not, in appearance, as also in composition, unlike the scum occasionally met with on the surface of glasses produced from batches in which the alkali is present wholly as soda ash. It would be of interest to know if those manufacturers who have been troubled most frequently with this scum have used arsenious oxide in the batch.

At the present time we are at a loss to suggest an adequate reason for the appearance of this scum. One might suppose that fine particles of sand were carried to the surface by escaping arsenious oxide; but the amount of the latter which was lost was very small. It has already been stated that with the 56 lb. pots no scum was found. As mentioned in the next section, however, there is reason to believe that despite the similarity of temperature in the furnace, the glass melted in the 56 lb. pots was at a uniformly higher temperature than the 100 lb. pots.

The Influence of Arsenious Oxide on the Refining of the Glass.

If arsenious oxide is retained in the glass it could only assist both in the melting and in the refining operations by

[18] See report on the influence of Moisture on the Rate of Melting and other Properties of Soda-Lime Glasses.

a marked reduction in the viscosity and in a reduction in the melting point of the other constituents. It could not exert the mechanical effect generally believed to be associated with its use since practically none of it is removed by volatilisation.

The practical melting operations confirmed this view. All the glasses of the series contained fine seed at the end of the melting operation. Since, however, some of the glasses made from the same batch containing moisture but no arsenic were obtained free from seed within the same melting period as was allotted to the arsenic-containing glasses, we were forced to conclude that under the conditions of our experiments arsenious oxide did not materially assist the refining operations. There was no evidence of a boil in the glass at any stage, the seed appearing in a fine condition from the outset. The boiling effect usually attributed to arsenic was never in evidence.

The glasses melted in 56 lb. pots were, generally speaking, freer from seed than those melted in the 100 lb. pot. The glasses melted in the larger size pot have already been referred to as bearing a scum. Both furnaces were operated at the same temperature, but as the 56 lb. pot had a smaller diameter than the 100 lb. pot, the glass at the centre might be expected to have a slightly higher temperature than in the larger vessel. It is probably, then, to the existence of a slightly higher temperature inside the 56-lb. pots that the greater freedom from seed is to be attributed, certainly not to the presence of arsenious oxide, which was associated with an increase rather than a diminution in the amount of seed.[19]

The Influence of Arsenious Oxide on the Colour of Soda-Lime Glasses.

The results of the observations on the effect of arsenious oxide on the colour were quite definite.

Beginning with the glass from the batch containing 1 part of arsenious oxide per 1000 of sand, the glass pro-

[19] See also Silverman's contribution to the discussion on paper by F. Gelstharp, Trans. Amer. Cer. Soc., 1913, 15, 585. Compare also Frink, Trans. Amer. Cer. Soc., 1915, 17, 798.

duce had a pale bluish-green colour definitely paler than the corresponding glasses produced without arsenious oxide. When two parts of arsenious oxide were present per 1000 of sand, the colour of the glass was pale green with a tendency to yellowish-green, the depth of colour being distinctly less than when only one part of arsenious oxide was added. Improvement in so far as reduction of colour was concerned occurred continuously throughout the series, the glasses made from a batch with 10 parts of arsenious oxide per 1000 of sand having only a very pale green tint.

These results were quite confirmed by a series of small scale meetings in which the amounts of arsenious oxide were raised from 20 up to 250 parts per 1000 of sand. Side by side with these meltings, one was carried out in which *no* arsenious oxide was present. The effect of arsenious oxide in removing the green colour was then very definitely apparent.

There does appear to be justification, therefore, for the view that whatever other useful function arsenious oxide may or may not exert it does tend to reduce the depth of the green tint produced by iron oxide. It is quite possible that this reduction in colour is due to the formation of ferric arsenate, which is practically colourless.

The first glass of the series made from a batch containing only 1 part of arsenious oxide per 1000 of sand was the only one having a bluish tint. We have in practice frequently employed arsenious oxide for the purpose of removing the bluish tint which glasses acquire when melted under certain conditions.

General Conclusions.

It will be seen that, as the result of the work recorded in this paper, a number of traditional beliefs would appear to have no foundation. Thus, the general view that arsenious oxide when added to the glass batch is entirely or almost entirely eliminated during the process of melting and refining is entirely erroneous. So different is this belief from actual fact that instead of the arsenious oxide being eliminated we have found that with batches containing one and two parts of the oxide per 1000 of sand, practically all is retained;

whilst there is no very considerable loss until amounts are added far beyond those used in practice. Thus, with 200 and even 250 parts of arsenious oxide per 1000 of sand we found in some cases as much as 60 per cent. of the arsenic retained.

As the result of these experiments we may also regard as settled that a considerable proportion of the arsenic is converted into the form of arsenate. The proportion of the residual arsenic as arsenic oxide was in the majority of cases more than one half. It varied in a somewhat irregular manner, but it is to be noted that when large amounts of arsenious oxide were added the residual pentoxide was never less than about 60 per cent. of the total, and in some cases exceeded 70 per cent. Under the conditions of our experiments, that is to say, with covered pots and with no oxidising or reducing agents present, we have shown that both forms of oxide were present; the proportion of the arsenic oxide preponderated as a rule.

Not only have we shown that arsenious oxide used in a glass batch is to a very large extent retained in the glass, but that the beliefs that it acted as a flux and further that it assisted in the refining process cannot be sustained. Indeed, it has quite definitely been shown that the corresponding batch without arsenic present melted at a lower temperature than those containing large quantities of arsenious oxide. The only sense in which the material could be said to act as a flux is that when sufficiently high temperatures are employed to melt the glasses, those containing a large amount of arsenite or arsenate are more fluid than the glass free from arsenic. This result is not surprising since the phosphates and borates containing large amounts of phosphoric oxide and boric oxide are also fluid, being unlike the silicates in this respect. Moreover, the reduction in the proportion of silica through the addition of large amounts of arsenic will of itself naturally tend to produce a more fluid glass quite apart from any action of the arsenic itself.

Only in its action in effacing the green or the blue colour of iron oxide-containing glasses has a useful function for the arsenious oxide been proved. In the face of these results, one is bound to raise the question again as to

whether the addition of arsenic to a glass batch is not superfluous. Except for the possible beneficial effect on the colour our results lead us to the belief that in making soda-lime glasses the addition of arsenious oxide is entirely unnecessary when the glass is melted in pots, and its omission would result in distant saving in the cost of the batch. In the case of tank melted glass it certainly appears to be wholly superfluous with the possible exception of its addition with selenium as a decolouriser. Even in this case there is a suspicion that in glasses in which the source of alkali is wholly soda ash, the presence of arsenic may even be responsible for the formation of the siliceous scum occasionally found unmelted on the surface.

Before finally condemning arsenious oxide as a general batch ingredient it does appear desirable to investigate a little more fully its effect in lead-oxide containing glasses, and the result of varying furnace conditions corresponding to oxidising and reducing effects. While we must await the conclusion of experiments of this kind we must certainly bear in mind that in glass used for lampworking purposes arsenic has already been proved to give rise to discolouration when worked. It should, therefore, be absent from glass which is to be used for drawing into rod and tubing.

There is another important consideration, namely, in the case of glasses used for food preserving and for chemical purposes, as to whether or not the arsenic retained in the glass is extracted by the contents sufficiently to have any deleterious effect. We ourselves rather take the view that the extraction of arsenic from a glass container by any preserved food placed in it is bound to be infinitesimal and negligible if the glass itself is of durable quality, and the only likely danger would arise from the use of a glass which underwent rapid weathering. As the batches which are used now-a-days for the production of colourless glass in tank furnaces almost always contain arsenious oxide, to an extent up to about 3 parts per 1000, it is rather desirable that the problem should be investigated. In the case of chemical and scientific glassware containing the oxides of arsenic it is

quite within the bounds of possibility that an alkaline solution could extract sufficient material from the glass to be capable of a positive result when some delicate test for arsenic like the Marsh test is applied.

This problem of the extraction of arsenic from glass is one which, in our opinion, should be given early attention in order that there should be no basis for a scare about the possible contamination of foodstuffs through arsenic derived from the glass.

Summary.

The foregoing investigations show that:

1. When arsenious oxide is present in a soda-lime batch, and the latter is melted in covered pots at a temperature of 1400°, practically the whole of it is retained when the amount so added is about one to two parts per 1000 of sand, whilst 60 per cent. or more is retained even when 250 parts per 1000 are added.

2. Under the conditions of our experiment, with no oxidising material present, from 40 to 70 per cent. of the arsenious oxide retained in the glass was found to be converted to arsenic oxide.

3. No beneficial effect on the rate of melting has been found to be associated with the presence of arsenious oxide in the batch and with large amounts of the oxide a higher melting temperature is needed than without it.

4. The presence of arsenious oxide in amounts greater than two parts per 1000 of sand is liable in soda-lime batches to produce on the surface a scum containing a high proportion of silica.

5. Arsenious oxide when added to the batch in amounts up to 10 parts per 1000 of sand does not appear to exert any beneficial influence on the refining of the glass.

6. The presence of arsenious oxide does quite definitely reduce the green tint due to the presence of iron oxide. The green tint becomes paler and paler as the amount of arsenious oxide is increased.

7. Arsenious oxide when present to the extent of 150 to 250 parts per 1000 of the sand produces glasses of varying degrees of opacity.

8th January, 1923.

II. The Influence of Water on the Rate of Melting and on the Working of Lime-Soda Glasses.

A Report by the Department of Glass Technology, University of Sheffield, on Investigations carried out on behalf of the Glass Research Association.

Programme of Research, 1922-23.
Item 7(*c*).

Abstract: A considerable number of meltings in covered pots at 1400° C. have been made of soda-lime batches in which amounts of moisture varying from 0.25 to 10 or even 15 per cent. were present. Some batches contained soda ash only as the source of alkali, others varying proportions of soda ash and saltcake. It was found that the ultimate composition of the glass was not materially affected by the amount of moisture added to the batch. In general, the presence of moisture had a beneficial effect on the rate of melting. In the case of wholly soda ash batches, the best amount appeared to be 1 per cent., and the maximum to be used should not exceed 2 per cent. With saltcake present, 3—4 per cent. of moisture could be employed with advantage. Glasses made from moist batches appear to become stiffer or more viscous in working, and when 5 per cent. of moisture was added to soda ash batches the glass obtained was stiff and lumpy. These differences in working were noted despite the fact that the chemical compositions of the glasses were closely alike. The question of residual water in glass was discussed and emphasis laid on the need of obtaining some definite measure of the working qualities of a glass.

THE part which water may play both during the melting of a glass from batch and on its subsequent properties is a matter alike of practical and theoretical interest. The number of scientific problems concerned is very considerable, and although the dominant note in this communication is the practical, we have not failed to point out how needful, for the thorough understanding of the problems at issue, are additional fundamental researches which at first sight may appear only to be of academic interest.

The immediate practical problem will first be dealt with. For, having ascertained what was the influence of moisture on the thoroughness of batch mixing, it was desirable to find out whether or not moisture was beneficial also during the melting process.

It may be recalled that the effects of moisture on the batch, so far as can be stated from general knowledge, are divisible into two groups, the one group having undoubtedly unfavourable results on the rate of melting of glass, the other being of assistance both in connection with the mixing of batch and on the founding of the glass. To what extent these groups counterbalance or overbalance one another has had to be decided by experiment. The evidence in connection with batch mixing decided in favour of the presence of moisture within narrow limits. The tests and results on the rate of melting and refining will now be set out.

The Batches Tested.

In all the experiments recorded in detail in this communication, the types of batch used were those in such widespread use for the production of soda-lime glasses; for these cover both pot and tank furnace practice and have immediate importance for probably 90 per cent. of the glass manufacturers.

The soda-lime glasses are produced as a rule from a mixture of sand, soda ash and limespar (or other form of calcium carbonate), or from sand, saltcake and limespar (or limestone), or again, from sand, soda ash, saltcake and limespar. The second type of batch is used now very much less frequently than before the war, and as our own experiments were conducted in covered pots and we did not desire to add much carbonaceous matter to the batch for the purpose of reducing the saltcake, we confined our tests to the soda ash and the mixed soda ash and saltcake batches. Two sets of batches in each case were tested, the precise compositions being set out in Table I.

The second set of batches (II.) differ from the first (I.) in containing a greater amount of the basic constituents.

TABLE I.

The Batches Tested.

	No.	Sand.	Soda Ash.	Saltcake.	Limespar.	Coke.	Per cent. moisture. Separate.	Per cent. moisture. Average
I.	527a	1000	325	—	228	—	0.24, 0.25	0.25
	527b	1000	325	—	228	—	0.89, 0.83	0.86
	527c	1000	325	—	228	—	2.40, 2.47	2.44
	527c/2	1000	325	—	228	—	2.28, 2.41	2.35
	527d	1000	325	—	228	—	4.72, 4.74	4.73
	527d/2	1000	325	—	228	—	4.83, 4.89	4.86
	527e	1000	325	—	228	—	14.63, 14.89	14.76
	527e/2	1000	325	—	228	—	14.76, 14.58	14.67
II.	518a	1000	350	—	240	—	0.34, 0.36	0.35
	515b	1000	350	—	240	—		0.83
	515b/2	1000	350	—	240	—		0.81
	516a/3	1000	350	—	240	—	1.94, 1.84	1.89
	516a/4	1000	350	—	240	—	1.85, 1.87	1.86
	516a/2	1000	350	—	240	—	15.35, 15.05	15.20
III.	528a	1000	296	71	240	5	0 78, 0.86	0.82
	528a/2	1000	296	71	240	5	0.78, 0.88	0.83
	528b/2	1000	296	71	240	5	1.84, 1.94	1.89
	528b/3	1000	296	71	240	5		1.95
	528c	1000	296	71	240	5	4.00, 3.92	3.96
	528c/2	1000	296	71	240	5	4.05, 3.93	3.99
IV.	529a	1000	270	104	240	7	1.02, 1.21	1.12
	529a/2	1000	270	104	240	7	1.00, 1.15	1.08
	529b/3	1000	270	104	240	7		1.85
	529b/4	1000	270	104	240	7	2.10, 2.02	2.06
	529c	1000	270	104	240	7	4.32, 4.15	4.24
	529c/2	1000	270	104	240	7	4.22, 4.22	4.22
	529d	1000	270	104	240	7	9.87, 10.23	10.05

Similar batches may be met with in fairly common use in pot furnace practice, although they are somewhat stiffer and quicker setting than are now used on automatic machines. Nevertheless, they are of such types that the principles discovered in regard to the effect of water should be of general application.

Batches II., III. and IV. are related in the sense that the total alkaline oxide in the finished glass should be the same in all cases. Set III. is derived from II. by replacing a definite proportion of the soda ash by an equivalent of salt-cake, and this replacement is carried to a further stage in IV.

The methods of adding the moisture to the batches have been described in an earlier paper. As an ordinary " dry " batch in commercial practice will contain about 1 per cent. of moisture, special drying had to be accorded to the batches containing 0.25 and 0.35 per cent. only. These batches, after being prepared, were heated for seven hours at 180° to 200° in the container (about 50 lbs.), being stirred very frequently during the period. A further mixing was given after the period of drying. It will be noted that this lengthy period was not sufficient, with this large mass, to dry the batch perfectly.

In the experiments relating to the mixing of batch, there was no object to be achieved by proceeding beyond an addition of 6—7 per cent., for this amount was clearly detrimental to that process. It was thought a matter of interest, however, in connection with the experiments on melting, to test really wet batches, and hence amounts of approximately 10 per cent. and 15 per cent. were added in some cases. Each set does not cover precisely the same range of moisture, but there was sufficient repetition to afford confirmation of the results of importance.

The Chemical Composition of Glass in Relation to the Amount of Batch Moisture.

As throughout these experiments we were attempting to test the effect of moisture on the rate of melting and on various properties of the molten glass, it was necessary to

reassure ourselves that our conclusions were not complicated by any decisive differences in composition which of themselves would bring about differences in the properties of the glasses.

The complete analysis of each sample of glass was therefore carried out at *least in duplicate.* The mean values of closely agreeing results are recorded in Table II.

A note is necessary in regard to the SO_3 content of the glasses. In the series designated I. and II., the small amounts of SO_3 found present must have been absorbed from furnace gases and clearly no account can be taken of them in the calculated composition. To produce the other glasses, however, saltcake was added. If chemical action were complete and all the SO_3 expelled, the ultimate composition of the glasses in series II., III. and IV. should be identical. As a matter of fact, we know that SO_3 is retained, presumably the decomposition of the saltcake being incomplete. The amount undecomposed is not a fixed amount.* It becomes impossible, therefore, to calculate the ultimate composition of glass made from saltcake. We have indicated, in the table, the compositions which should finally be obtained, assuming that (a) all the saltcake has been decomposed with evolution from the glass of the SO_3, (b) all the saltcake remains unchanged. But whilst showing these values, we have taken as the basis for comparison the composition of the glass (*c*) containing the average amount of SO_3 for the whole series, the other constituents being calculated to the basis of (100-x) where x is the percentage of SO_3.

In view of the presence of SO_3 more extensively in glasses III. and IV. than in the others, we could not expect identity of composition between sets II., III. and IV.; but, as the average percentage of SO_3 present is not more than about two-thirds of one per cent., the compositions should not greatly vary.

On comparing the compositions in sets II., III. and IV. it will be seen that they are substantially the same. With

* See, for example, Gelstharp, Trans. Amer. Cer. Soc., 1912, 14, 665.

TABLE II.

The Percentage Compositions of the Glasses.

	No.	Moisture content of the batch	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	Total
I.	527a	0.25	75.10	0.26	0.10	10.48	trace	13.83	0.19	99.93
	527b	0.86	75.04	0.47	0.09	10.34	,,	13.99	0.15	100.08
	527c	2.44	75.06	0.24	0.08	10.71	,,	13.74	0.07	99.90
	527c/2	2.35	75.84	0.28	0.06	10.08	,,	13.63	0.14	100.03
	527d	4.73	75.48	0.40	0.08	10.34	,,	13.63	0.07	100.00
	527d/2	4.86	75.64	0.22	0.08	10.36	,,	13.56	0.08	99.94
	527e	14.76	75.44	0.13	0.07	10.14	,,	13.93	0.16	99.87
	527e/2	14.67	75.32	0.13	0.07	10.20	,,	13.93	0.15	99.80
	Calcd.	—	76.14	0.15	0.02	9.73	0.05	13.90	—	99.99
II.	518a	0.35	74.98	0.17	0.03	10.03	0.09	14.88	—	100.18
	515b	0.83	74.99	0.28	0.04	9.98	trace	14.63	—	99.92
	515b/2	0.81	75.40	0.34	0.06	9.68	,,	14.45	0.08	100.01
	516a/3	1.89	74.12	0.40	0.08	10.00	,,	15.22	0.12	99.94
	516a/4	1.86	74.74	0.56	0.10	9.88	,,	14.63	0.03	99.94
	516a/2	15.20	74.82	0.56	0.06	9.61	,,	14.97	0.14	100.16
	Calcd.	—	75.09	0.15	0.02	9.81	0.06	14.87	—	100.00
III.	528a	0.82	74.86	0.30	0.09	9.58	trace	14.22	0.79	99.84
	528a/2	0.83	75.12	0.22	0.06	9.72	,,	14.09	0.73	99.94
	528b/2	1.89	74.52	0.28	0.10	9.74	,,	14.94	0.57	100.15
	528b/3	1.95	74.60	0.32	0.08	9.70	,,	14.48	0.67	99.85
	528c	3.96	74.24	0.43	0.07	9.92	,,	14.54	0.83	100.03
	528c/2	3.99	74.43	0.30	0.06	9.95	,,	14.77	0.71	100.22
	Calcd. (a)	—	75.14	0.15	0.02	9.87	0.05	14.77	—	100.00
	(b)	—	72.95	0.14	0.02	9.58	0.05	14.33	2.92	99.99
	(c)	—	74.62	0.15	0.02	9.79	0.05	14.66	0.72	100.01
IV.	529a	1.12	74.91	0.36	0.04	9.84	trace	14.05	0.60	99.83
	529a/2	1.08	74.82	0.77	0.05	9.60	,,	14.22	0.67	100.13
	529b	1.85	74.83	0.43	0.07	10.12	,,	13.26	0.84	99.52
	529b/2	2.06	75.76	0.76	0.06	9.64	,,	13.32	0.48	100.02
	529c	4.24	74.78	0.46	0.06	9.75	,,	14.31	0.68	100.04
	529c/2	4.22	75.04	0.42	0.08	9.86	,,	13.92	0.64	99.96
	529d	10.05	78.14	0.28	0.07	8.91	,,	11.86	0.52	99.78
	Calcd. (a)	—	75.33	0.15	0.03	9.83	0.05	14.59	—	99.98
	(b)	—	72.16	0.14	0.03	9.42	0.05	14.00	4.22	100.02
	(c)	—	74.88	0.15	0.03	9.77	0.05	14.50	0.60	99.98

the exception of glass 529d, which is so much higher in silica and correspondingly lower in the bases soda and lime than the other glasses that it must accordingly be excluded from comparison, all the other glasses are sufficiently close in

composition as to give one confidence in instituting comparisons.

In the individual series there is quite good general agreement. Thus, in series I., out of eight glasses, the extreme values for the silica are 75.02 and 75.84 per cent.; for the sodium oxide 13.56 and 13.99; for the calcium oxide 10.14 and 10.81. Similar good agreement is found in the other series.

Thus, we may conclude, as a general observation, that the ultimate composition of the glass is, for practical purposes, independent of the amount of moisture present in the batch. In this connection, attention may be directed to the glass 516a/2, made from a batch containing 15 per cent. of water. The actual composition found was almost identical with that calculated.

Having made this general statement, however, it is desirable that sight should not be lost of certain fairly definite tendencies. It will be noted that the amount of alkali present in the glasses very closely agrees with the calculated values. In regard to the calcium oxide, this was frequently found present in greater amount than calculated, whilst the silica, on the other hand, was usually distinctly less than the expected value. Except in series III., where the percentage of silica decreased and that of both bases increased, there was no regular variation with progressive increase in the amount of water in the batch, and we have no clear reason, therefore, to depart from our general conclusion that, in the production of soda-lime glasses, the ultimate composition is either not affected or is very little affected by the amount of moisture in the batch.

The Influence of Moisture in the Batch on the Rate of Melting and Refining of Soda-Lime Glasses.

The standard temperature of melting adopted was 1400°. The scale of operation included both 28 lb. and 56 lb. pot melting, and the results in both cases were substantially the same.

Before charging in the batch, the pot was fired in the furnace at 1400° for at least 12 hours subsequent to the pot arching. This is our almost invariable practice. After the first large charge of batch, the latter was allowed to melt down, the approximate time being noted.

It is not easy to control experimental tests of melting rate except on a laboratory scale. In the latter case it is always possible to remove a small crucible at the end of a specified interval and to examine the state of its contents; but with a large crucible, the frequent removal of the stopper to obtain samples may cause irregularities of temperature which interfere with the tests.

The data given below, therefore, must be understood to be approximate. In a number of cases the numerical results are the same, although, as the amount of moisture was different, different melting rates might have been expected. This similarity is probably due to the fact that the stopper could not be removed often enough to determine the difference. But whilst there is no differentiation between the glasses in each test, the evidence is sufficient, when all four tests are taken together, to point to certain definite conclusions.

One expected effect of the presence of moisture is a retardation of the melting, due to the heat consumed in volatilising the water. Hence, the time T_1 was noted, approximately, for the first large charge to melt down.

Next, the final disappearance of the batch after the second charge may be expected similarly to be dependent on the moisture present. A check on this was made by noting the approximate time (T_2) after the second filling at which the last traces of batch were seen and the time (T_3) also after the second charge when all batch was absent.

Similarly, observations were made on the disappearance of seed, the time T_4 being that subsequent to the second charge when the glass was entirely or practically free from seed, or when observations showed seed still to be present.

The times recorded are in minutes.

TABLE III.

	Glass No.	Per cent. Moisture in batch.	T_1	T_2	T_3	Rate of Melting and Fining. T_4
I.	527a	0.25	60	60	75	570 (little change after 270)
	527b	0.86	60	45	60	600
	527c	2.44	60	105	120	*600 Almost seed free (recurred after 840)
	527c/2	2.35	60	105	120	*Not seed free
	527d	4.73	100	105	120	Almost seed free at 570
	527d/2	4.86	100	105	120	,, ,, ,, 570
	527e	14.76	110	105	120	570 Nearly seed free at 300
	527e/2	14.67	110	105	120	570 ,, ,, ,, 300
II.	518a	0.35	90	240	270**	Seed throughout; worst of series
	515b	0.83	75	60	75	Fine seed throughout, but very small in extent
	515b/2	0.81	75	60	75	,, ,, ,, ,,
	516a/3	1.89	90	115	135	,, ,, ,, ,,
	516a/4	1.86	90	115	135	,, ,, ,, ,,
	516a/2	15.20	110	240	300	,, ,, ,, ,,
III.	528a	0.82	60	90	120	300 Nearly free
	528a/2	0.83	60	90	120	300 ,, ,,
	528b/2	1.89	60	105	120	360 Very nearly free
	528b/3	1.95	60	105	120	Traces after 20 hours
	528c	3.96	60	90	120	180
	528c/2	3.99	60	90	120	180 — Surface boil
IV.	529a	1.12	90	240	240-300	500
	529a/2	1.08	90	240	240-300	300
	529b/3	1.85	75	105	120	180
	529b/4	2.06	75	105	120	240
	529c	4.24	75	60	70	120 Tendency for seed to recur
	529c/2	4.22	75	60	70	240
	529d	10.05	90	240	300	720-780

* Temperature changes through temporary breakdown of blower were responsible for these higher figures.
** Stony inclusions.

The results, when all factors are considered, are fairly conclusive. Thus, when specially dried batches were tested, containing only about one-quarter or one-third of one per cent. of moisture, the time required to prepare glass in a fit state

for working was greater than when the normally dry batch (that is, with approximately 1 per cent. of water) was melted. So much is quite clear.

When still greater amounts of moisture were present, there appeared a differentiation between the batches made wholly from soda ash and those containing a mixture of soda ash and saltcake. In the former, the beneficial influence of moisture appeared already to have reached its maximum in the neighbourhood of 1 per cent.

It was otherwise when saltcake was present. As a rule, such batches melted down quicker than the corresponding soda ash batches, whilst the effect on the rate of refining was marked. Despite the deviation in the case of glasses 528b/2 and 528b/3, both with about 2 per cent. of moisture, it may be said that quicker melting and refining were obtained as the moisture was increased up to 4 per cent.

These general results having been set down, a note or two on the course of the melting in one or two special cases may be added. Thus, with the soda ash batches of series I., those containing more than 2 per cent. of moisture were very boily for some hours after the batch had melted down, the batch with approximately 5 and 15 per cent. respectively of moisture containing huge blisters. These observations, whilst they do not prove, do at least suggest that water is retained in the glass up to a high temperature, and is, in its later stages, but slowly given off. Some experiments to test the evolution of the gas from stage to stage were put in hand, but were again temporarily set on one side in order that the main problem might be proceeded with. It should be of interest to have these tests carried out.

It was noteworthy that in the case of the saltcake-containing batches, the formation of large boils and blisters following the melting down was rather less marked than with the soda ash batches. Whether or not this may be associated with some chemical action in the case of the saltcake batches or is due to the somewhat greater viscosity cannot be stated. So far as the individual substances soda ash and saltcake are concerned, we know that the latter is

dehydrated much more readily, namely, at 34°C, than the former, which must be heated to 100°C before losing its combined moisture. On the other hand, soda ash begins to react with silica certainly at 800°C* and probably below†, whereas saltcake requires a temperature of 1200° when it is present alone in contact with silica. Whether or not moisture is retained by these salts at such high temperatures, and whether and in what manner the moisture influences the decomposition of each, are problems which remain yet to be solved.

The Influence of Moisture in the Batch on the Working Properties of the Glass.

There still remain several other considerations before arriving at a judgment in regard to the influence of water present in a glass batch. For, whatever advantage moisture may have from the point of view of mixing, if its influence on the quality of the finished glass is detrimental, then clearly it should either not be added at all or the batch should contain only the minimum amount of moisture.

Three properties in particular concern us here, namely, the production of waviness, the tendency for seed or boil to reappear in the glass after once being refined, and finally the working properties of the glass.

It is not possible to set down any numerical values which precisely define the extensiveness of waviness or seed; or even the ease of working. It will mark a very great advance when viscosity measurements, for example, have been made on glass at high temperature; especially glass prepared from batches treated in different ways such as has been done in this investigation. For the time being we can only fall back on the general statements of the experienced glass worker whose business it was to work out the glass. Terms such

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* J. W. Cobb, J. Soc. Chem. Ind., 1910, 29, 69, 399.

† M. W. Travers, J. Soc. Glass Tech., 1921, 5, 68. D. Turner and W. E. S. Turner also communicated to the Feb. meeting, 1921, Society of Glass Technology, the results of investigations, showing that sodium carbonate extensively reacted with fireclay at 800°, whereas with saltcake reaction was very slight.

as " good working " and " quick setting " ought scientifically to be referred to some standard, but they will, nevertheless, be understood by the average glass maker. The term " sweet " is one which still waits clear definition. It probably refers to a glass which is thoroughly homogeneous.

In order that a ready review of the results may be obtained, they have been cast in the form of a table which is given below (Table IV.).

TABLE IV.

The Effect on Working Properties.

No.	Per cent. Moisture in batch.	Wavinesss	Recurrence of Seed or Boil.	General Remarks.
527a	0.25	2 Very slight	None	Working good. Quick setting
527b	0.86	,, ,,	Recurred slightly	,, ,,
527c	2.44	1 None	Recurrence due to change of temperature	,, ,,
527c/2	2.35	,,	,, ,,	,, ,,
527d	4.73	,,	,, ,,	,, ,,
527d/2	4.86	,,	,, ,,	,, ,,
527e	14.76	(3) Very distinct	Slight during last three hours	Viscous, lumpy and cordy
527e/2	14.17	(3) ,, ,,	,, ,,	
518a	0.35	2 Trace	Never free from seed	Worked well—sweet
515b	0.83	1 None	,, ,,	,, ,,
515b/2	0.81	None or very slight	,, ,,	,, ,,
516a/3	1.89	None	,, ,,	,, ,,
516a/4	1.86	,,	,, ,,	Stony glass. Easy to work
516a/2	15.20	(3) Distinctly cordy	,, ,,	Difficult to work. Viscous. lumpy and cordy
528a	0.82	None	None	Strong, viscous, easy working
528a/2	0.83	,,	,,	,, ,,
528b	1.89	,,	,,	,, ,,
528b/2	1.95	,,	,,	,, ,,
528c	3.96	,,	,,	,, ,,
528c/2	3.99	,,	,,	,, ,,
529a	1.12	,,	,,	Sweet and easy to work
529a/2	1.08	,,	,,	,, ,,
529b	1.85	,,	,,	,, ,,
529b/2	2.06	,,	,,	Strong, and easy to work
529c	4.24	,,	,,	,, ,,
529c/2	4.22	,,	Slight recurrence	,, ,,
529d	10.05	,,	,, ,,	Viscous and lumpy

The numbers attached to the description under the heading "waviness" represent the order of increasing waviness.

Once again the glasses can be differentiated without any difficulty. Those glasses made from very dry batch, that is, containing only 0.25 and 0.35 per cent. of moisture, do not appear in so unfavourable a light as when judged by other tests. There was, however, in both of them a very slight tendency to waviness, whereas such waviness was non-existent when a moderate amount of moisture between 1 and 5 per cent. was present. In the case of the saltcake-containing batches, waviness was not found in any of the glasses, whatever the moisture content.

Recurrence of seed does not serve so well as a basis of differentiation. It is possible to make the general statement that up to 3 or 4 per cent. of moisture in the batch, boil or seed did not recur, but was noticed on one occasion with a saltcake-containing batch having 4.22 per cent. of moisture. The recurrence of seed in the batches of series I. was rather due to an accidental fall in temperature than to the moisture content. When the batch, however, contained a large proportion of moisture, then recurrence of seed was a definite feature.

Between the working properties of the glasses made from soda ash and those prepared from saltcake alone or from a mixture of soda ash and saltcake, there exists a well defined difference known to all practical glassmakers, quite apart from the influence of water. The saltcake-made glasses are somewhat more viscous. We have found, in both cases, however, that the viscosity appears to increase (as tested by the behaviour of the glass when worked on the marver and drawn into tubing) as the moisture in the batch increased. Up to a certain stage this increase is not detrimental, but when that stage is reached a peculiar effect becomes noticeable, namely, that not only is the glass stiff in working, but seems to contain lumps or nodules. The general effect, to use the glassmaker's description, is that of trying to work a stiff rice pudding rather than of something thoroughly plastic, such as a good glass should be. When

glass tubing is drawn from such glass, it contains what one may describe as knots.

The stage at which the phenomenon was noticed was at approximately 5 per cent. of moisture in the soda ash batches. With a little more than 4 per cent. in the mixed soda ash-saltcake batches it was scarcely noticeable; possibly at 5 per cent. it might be apparent—we did not test. Certainly at 10 and 15 per cent. both types of batch gave glass which works very irregularly.

General Conclusions.

On reviewing all the evidence, fairly definite conclusions can be drawn. In the first place, it can definitely be stated that the presence of a small amount of moisture in a batch for preparing soda-lime glasses is an advantage, both in mixing and in melting.

The amount of moisture actually to be recommended differs according to whether the batch is prepared from soda ash alone or contains saltcake.

In the case of the soda ash batches, best mixing, as tested by analysis, was obtained when the batches contained about 3 per cent. or not more than 4 per cent. of moisture. Quickest melting and refining were got with batches having about 1 per cent. of moisture, whilst good working, absence of waviness and of secondary boil could be counted on at any point of the range 1 to 3 or 4 per cent. of moisture. On the other hand, with about 1 per cent. of moisture or less, segregation of the batch constituents was liable to occur.

There is obviously some room for compromise. The practical man may choose, if he has an efficient furnace, to make sacrifice slightly on the melting rate in order to make sure of good mixing; or he may be satisfied with a slightly less thorough mixing than we have shown in our tables is possible with 3—4 per cent. of moisture in the batch in order to get quicker melting and refining.

In any case we would lay down as a general rule that, with soda ash batches, the amount of moisture should not exceed 3½ per cent.; whilst as a general compromise we would advocate 1½—2 per cent. This quantity is quite

sufficient to prevent segregation of the batch materials and is not far removed from the amount which produces quickest melting and refining. Still further, the analytical results obtained as a test of batch mixing, although not quite so good as obtained with 3—4 per cent. of moisture, were on the whole satisfactory.

The case when saltcake is present is clear. Thoroughness of mixing and rate of melting and refining all indicate approximately 4 per cent. as the most suitable and beneficial amount of moisture to employ.

The Presence of Water in Glass.

Some of the results found during the course of this investigation once more raise the question of the presence of water in finished glass. The evidence on this subject is not in entire agreement.

Apart from any special additions of water to the batch, such as have been made in experiments related above, water vapour is always present in the products of combustion formed in a furnace, and on physico-chemical grounds one would expect absorption of some definite, if minute fraction, in the molten glass. It could be argued that the boil observed when a piece of metallic iron is dropped into molten glass is due to the presence of traces of water which, by reaction with the iron, yield hydrogen.

In 1916 Mr. S. English in the writer's laboratory began experimental work on the presence of gases in glass. From the preliminary experiments made, up to the softening point of glass, it appeared that gas was actually evolved before fusion occurred and that moisture was predominant, but the investigation has not been completed.

Some time later, in 1917, Sir Herbert Jackson informed the writer that his own experiments on the extraction of gases from glass led him to the conclusion that water formed the main constituent. Later, in an address to the Society of Glass Technology, Jackson* stated his view that without traces of water, the devitrification of glass, especially of borosilicates, did not occur. These same views were repeated

* J. Soc. Glass Tech., 1917, 1, 143.

in 1919† in a lecture on glass and its problems; whilst in a more recent paper§ he stated that the presence of moisture may influence annealing, and in the case of a borosilicate, perfect annealing was practically impossible when water was held in solution.

As the result of experimental work carried out at Corning, Sherwood in 1918** came to the conclusion that there were two distinct types of evolution of gas, the one resulting from absorbed gases and the other from the decomposition of the glass or evolution from gas in solution. Absorbed gas was readily removed, he believed, at a temperature below 300°. The further evolution of gas depended on the softening point of the glass and might be important at 400° for the softer glasses or not until 500° for the harder ones. In the second stage, water, carbon dioxide, carbon monoxide, hydrogen and nitrogen were eliminated, water predominating.

In regard to the influence of annealing, Sherwood found that if a glass vessel had been annealed at a certain temperature, and subsequently re-heated, there was practically no evolution of gases until this annealing temperature had been passed.

Ulrey|| has also found that annealing at ordinary pressure reduces the amount of gas which can be removed by subsequent heating in vacuo.

One is reminded, in this connection, of the increased evolution of gas which takes at the transition points in iron and steel, especially in view of Tool and Valasek's confirmation of heat absorption or evolution over the softening or setting range of glass.

How far the presence of moisture affects analytical figures representing compositions of glass cannot be stated definitely. It is pretty clear, however, that the amount of moisture remaining in glass after melting, certainly between 1300° and 1400°, cannot be more than a small fraction of one per cent.

In view of the experiments of English, Jackson and Sherwood, and in view of the general experience that the

† J. Roy. Soc. Arts, 1920, 68, 134.
§ Trans. Faraday Soc., 1920.
** J. Amer. Chem. Soc., 1918, 40, 1645.
|| Phys. Review, 1919, 14, 160.

total oxides found by analysis are more often slightly less than slightly in excess of 100 per cent., it does look as if there were some undetermined factor present only in small amount, and it may be water and dissolved gases which cause the discrepancy as well as traces of Cl, SO_3, TcO_2 and other groups seldom taken account of.

The actual loss which occurs on heating glass is very small. For the purpose of testing this loss, samples of glass were prepared for analysis and the loss in weight determined at different temperatures. Two glasses, designated 516a and 518a, made from the same batch, namely,

Sand 1134,
Soda 396,
$CaCO_3$ ... ... 270, were used in the test.

In the one case the batch materials were dry, in the other the batch had a total 10 per cent. of moisture added.

The changes in weight referred to were calculated as percentages on the material dried at 110°C. At each temperature one period of heating of two hours' duration was given. The results were as follows :—

	No. 516a (Wet)			No. 518a (Dry)			
Temp.	Loss on ign. of material.	% loss at each temp.	Cumulative % loss	Loss on ign. of meterial.	% loss at each temp.	Cumulative % loss.	Remarks.
110°C.	0.2 mg.	0.0293	0.0293	0.1 mg.	0.0100	0.0100	Dried in air oven
400°C.	1.1 ,,	0.1171	0.1464	1.0 ,,	0.1096	0.1196	Electric muffle
500°C.	—	—	0.1464	0.2 ,,	0.0200	0.1396	
600°C.	0.1 ,,	0.0098	0.1562	0.2 ,,	0.0200	0.1596	
700°C.	0.2 ,, yellowish white	0.0293	0.1855	0.1 ,, bluish white	0.0100	0.1696	Dull red heat and glass showed incipient fusion
800°C.	0.2 ,,	0.0195	0.2050	0.2 ,,	0.0200	0.1896	
900°C.	0.3 ,,	0.0380	0.1670	0.2 ,,	0.0200	0.1696	N.B.—Increase in weight
920°C.	0.3 ,, bluish white	0.0380	0.2050	0.2 ,, bluish white	0.0200	0.1896	Decrease in weight which equalised increase at 900°C.

The question of the nature of the loss in weight at each stage does not arise; the point of importance is that there is only a loss at 920° of 0.02 per cent. more from the " wet " glass than from the " dry."

In another test carried out at temperatures up to 330° and a pressure of 3—4 m.m., the actual losses of both " wet " and " dry " glasses (after preliminary drying at 105°) were identical at the end of 22 hours' treatment, the total loss being very small.

In the experiments of Washburn, Footitt and Bunting,* in which various kinds of glass were melted at a high temperature and the gases dissolved extracted under reduced pressure, the total weight of oxygen, carbon dioxide and nitrogen evolved by a barium flint glass was 0.046 per cent. and by a borosilicate 0.01 per cent. It is noteworthy that these investigators make no reference to the presence of moisture.

In the uncertainties arising after a perusal of the work of the several investigators referred to, there is suggestiveness in some of the results recorded by us during the working of glasses made from batches containing moisture. We have already referred to the presence of boils and blisters for some hours by the molten glass prepared from wet batches. The fact that they appear is associated with water, although we have not demonstrated that such blisters consisted or even contained water. The peculiar working properties of the glasses made from wet batches do clearly suggest, however, that water is present. For one of the glasses made from a batch containing 15 per cent. of moisture is almost identical in composition with the calculated value; and in no case can the phenomena observed be ascribed to an unworkable or difficultly workable composition. The observation only serves to whet the interest for further accurate investigation on the amount of water retained by glass.

* University of Illinois Bulletin, 1921, No. 118.

III. Purification of Gas.

(Report of Investigations carried out by Members of the Staff of the Glass Research Association.)

Programme of Research, 1922-3.
Item 8c.

Abstract : Investigation of the causes of bloom on glass worked in a lamp or otherwise finished by gas flame. The main cause found to be sulphur in the gas. This sulphur exists as compounds not easily removed. Description of experiments whereby it was shown that even very minute traces of sulphur produce bloom. Description of a catalytic method of removal and the type of apparatus required.

THIS problem was originally undertaken on behalf of the lampworking section of the Industry. The appearance of bloom, devitrification and other forms of clouding of glass when tubing is worked in the lamp flame, called for investigation as to the causes. It has been determined that clouding of whatever character is related to the purity of the gas employed in the lamp. It followed naturally that the research as to causes went hand in hand with attempts to remove the objectionable impurities, the determination of their nature and the minimum amounts which could be considered innocuous. That is to say, the problem necessarily involved acquaintance with the properties of glass together with careful practical experiments in gas treatment.

The main impurity which affects the glass is sulphur. It has been found that while some tubing would cloud readily in gas containing small quantities of sulphur compounds and other kinds of tubing not so readily, all would cloud upon repeated re-heating whenever the gas contained sulphur in any form. Presumably all sulphur compounds in gas yield sulphur dioxide in the flame which may form insoluble sulphites or sulphates in the glass along the margin of impact where the temperature

is not high enough for their absorption. However this may be, our problem is to remove the sulphur.*

The results we have obtained may prove to be of much wider application than was originally anticipated, for not only the clouding produced in lampworking but also the dimming and bloom which occur in the fire-finishing of tumblers, etc., result from the same cause.

Crude coal gas contains per 100 cubic feet something like 600 grains of sulphur in various forms. The bulk exists as hydrogen sulphide and this is almost entirely removed at the gasworks. The ordinary town supply contains about 28 grains of sulphur per 100 cubic feet, existing as carbon disulphide and other organic compounds which are very difficult to deal with.

There are two general methods of attempting the removal. One is to find a substance which will absorb the sulphur compounds directly; the other, to pass the gas over a catalyst capable of converting all the sulphur to hydrogen sulphide which is easily absorbed.

Our early attempts followed the first method and were very useful in discovering means of testing the different glasses and proving that sulphur was indeed the cause of bloom.

Ferric hydroxide heated to 250°C was found to absorb practically all the sulphur, but its life was short and its preparation on the large scale would be troublesome. Cobalt oxide was then tried at the same temperature with better success. Numerous difficulties were met with. The procedure for preparing the material was that adopted for its use in a quite different process. (Jour. Amer. Chem. Soc. 43, No. 9. September, 1921, p. 1982.) With this material temperature control gave a good deal of trouble and progress was slow. At that time, we could only

* More than twenty years ago practical work in America had led to the discovery that sulphurous fuel damaged the surface of glass in the lehr. Conclusive tests as to the fact of sulphur in an oxidizing atmosphere producing a film on hot glass had been made in 1904 by G. T. Beilby and were described in "The Chemical News," Vol. 90, No. 2,341, Oct. 7, 1904.

get the cobalt oxide to absorb 5% of its weight of sulphur, which meant that a pound of material was necessary to treat 1,000 cubic feet of gas. Even allowing a fair recovery value for the used cobalt oxide this meant doubling the price of the gas. All attempts at revivifying the cobalt absorbent short of re-dissolving and re-precipitating were unsuccessful.

In the course of these experiments we were led on to heating the cobalt-oxide to higher temperatures with the result that it was reduced to metal and acted catalytically, converting about 90% of the total sulphur to hydrogen sulphide. That is to say, the sulphur in the gas was reduced from 28 grains to something like 3 grains per 100 cubic feet. (Analyses of the gas could not be undertaken, but quantitative determinations of the sulphur extracted were repeatedly made, using cadmium as precipitant. The figures thus obtained were compared with the official analysis of gas supply.)

Having now a means of removing a large proportion of the sulphur we were able to form a fairly definite idea of the quantities operative in producing bloom. It appears that for the most exacting of lampworking conditions, perceptible bloom will be caused by a content of sulphur of a fraction of one grain per 100 cubic feet. For articles which are not in the flame for more than a minute 1 or 2 grains will not cause appreciable bloom.

All the foregoing experiments were on a laboratory scale, dealing with at the most 4 cubic feet of gas per hour. The best results were obtained by using the catalyst in one tube, removing the hydrogen sulphide by passing through a solution, and re-treating the gas in a second tube containing cobalt oxide absorbent at 250°C.

A larger apparatus capable of supplying one full-sized blow-pipe was constructed on this double principle. It was hoped that the life of the cobalt absorbent would be long, since the bulk of the sulphur was removed in the first tube. In practice this did not prove to be the case, or, at any rate, the absorbent gave trouble in various ways. The double treatment was then modified using two catalyst tubes with cobalt reduced to metal and heated to 700°C. The suggestion was made that owing to

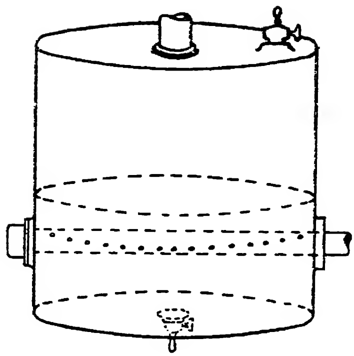
mass action in the first tube the hydrogen sulphide concentration could not exceed a certain degree without reverse action taking place, and this view was upheld by experiments in varying the rate of flow. Slow passage of the gas over the catalyst gave worse results than a more rapid flow.

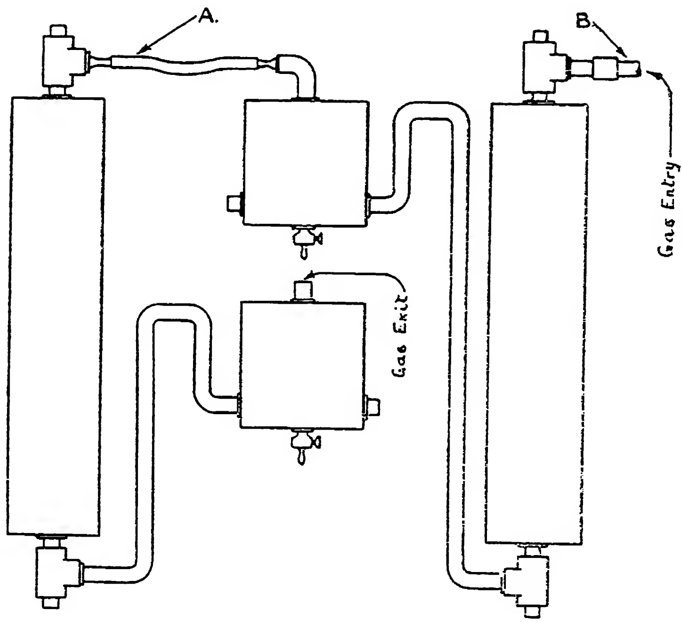
A larger apparatus using two electrically heated tubes containing firebrick coated with catalyst was next tried. In order to be able to treat a fair quantity of gas, enough for several blowpipes in a lamp working shop, it appeared necessary to use a compressor. The friction was considerable in the apparatus as evolved from the smaller ones which worked quite well with the ordinary pressure. A satisfactory compressor was difficult to obtain at once and, of course, it would be preferable to avoid its use, if possible. As absorbent for the hydrogen sulphide a solution of commercial ferrous sulphate made slightly alkaline with caustic soda is cheap and efficient. The suitable concentration of this suspension depends somewhat upon the rate of flow of the gas as it is necessary that the bubbling should agitate the liquid. A 20% solution of ferrous sulphate, with the necessary caustic soda dissolved in an equal bulk of water, before mixing gave very good results.

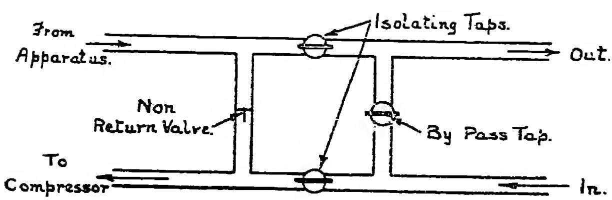
The best means of heating, of disposal of the catalyst in the container, the rate of flow, are all points which require further work, but we consider that these experiments have been most fruitful in leading to a better understanding of bloom, its relation to sulphur in the gas even in minute quantities, and in showing in broad outline what kind of plant may be used for purification.

The apparatus which was made on the double principle for actual trial in a lamp-working shop is shown in the accompanying sketch. Its capacity is 100 cubic feet per hour, assuming an average sulphur content of 28 grains per 100 cubic feet.

The catalyst tubes are of $1\frac{1}{2}''$ gas barrel, $36''$ long, wound with $.051''$ nichrome wire. Insulation from the iron pipe is provided by a coating of pyruma cement followed by a spiral layer of asbestos paper. The correct current is intended to be 6 amperes (33 amp. turns per inch) with the winding cold. This falls to




A.
B.
Gas Entry
Gas Exit


From Apparatus.
Isolating Taps.
Out.
Non Return Valve.
By Pass Tap.
To Compressor
In.

about 5 amperes as the temperature rises. The tubes are intended for use on a 200 volt circuit, and a small adjusting resistance is required. It would be wise to make an actual trial of the temperature under running conditions to ensure that it does not exceed 1,000°C in the hottest part. The winding is covered with a further layer of pyruma and the whole encased in an outer sheet-iron tube 4½″ diameter, the intervening space being filled with slag wool.

The washing tanks are 9″ diameter, 9″ high, of welded sheet iron. They are designed to be used half full of liquid. The gas is admitted by the perforated cross tube, which can, if desired, be removed for cleaning, and flows out of the central exit tube in the top. Taps are provided top and bottom for filling and emptying by means of rubber tubes.

The whole apparatus, connected up with ¾″ gas barrel, is housed in a framework of angle iron, all parts being removable, and their relative positions and connections are illustrated diagrammatically. As will be seen, the ends of the catalyst tubes are finished off with reducing T pieces, whose ends are closed with removable plugs for filling and emptying. To provide some freedom of the separate parts, "cold gas" connections, as at A and B are of rubber. It may be necessary to shield these from the hot air rising from the tubes, and in any case the apparatus should not be allowed to stand with no gas at all flowing, or overheating will occur. This is provided for by passing a constant current, regardless of consumption, by means of a compressor, surplus gas being allowed to pass, by a non-return valve, back into the entry tube. The whole apparatus can be isolated and the gas by-passed by means of three taps. (See diagram.)

It is evident that this apparatus is not of such a nature as would lend itself to construction in separate units attached to single blowpipes and must, therefore, be so installed as to treat the whole of the gas before distribution.

There is nothing further about the lay-out that is not quite obvious. As regards working, the catalyst tubes, once filled, require no attention. The first washing tank, removing the

bulk of the H_2S, requires emptying every day. It might last longer, but it is necessary to avoid using it after it has ceased to be efficient, as this reduces the efficiency of the second catalyst. The second washing tank should be emptied once a week.

Since the beginning of our investigations and upon making enquiry it has been found that the Carpenter-Evans Patents to a great degree satisfy the conditions which are required to remove the major portion of the sulphur compounds that would be detrimental in such work as the fire polishing of tumblers, etc. However, so far as we have been able to determine, the Carpenter-Evans Patents do not completely remove the last traces of compounds which produce clouding and bloom so that the gas so purified may under all conditions and with all kinds of tubing be used for lampworking purposes. However, for the average lampworking shop the Metropolitan Gas Co. have an equipment which will probably be sufficiently effective to fulfil most of the requirements, but in the event of members desiring to construct an apparatus it is believed that the directions and information given above are sufficient to enable them to do so. It would be our pleasure to give any assistance and furnish any designs required.

IV. Abstract-Report

of work upon refractories for Glass, carried out for the Glass Research Association by the Joint Committee of the British Refractories Research Association and the Glass Research Association.

Programme of Research, 1922-3.
Item 10 (a).

THE work under review occupied about eighteen months and was finished at the end of last year. To be of any real service the investigations had to be carried out on a works scale under commercial conditions. Throughout the whole course of the work efforts were made to adopt methods which would be suitable for economic development in the event of success, and consequently at different stages various modifications had to be introduced into the trial methods originally adopted. Also, it was decided to use definite proportions of graded grog. No combination of the crushing plant available gave satisfactory results, and it was necessary to resort to hand grading. As a result we were compelled to crush and grade about 28 tons of clay to obtain just under 25 cwts. of the grog. These facts, together with the time unavoidably taken up in weathering, souring and drying, and the economic conditions obtaining during the early stages of the work, are responsible for the delay in presenting the results of these important investigations.

The full results, of course, will not be ready until the blocks have been tried out under working conditions in our experimental tank furnance now under construction, but it is

considered that the results so far obtained justify the publication of this preliminary note.

The investigation was designed mainly with a view to determining the effects of varying quantities of free silica in clay materials, upon mechanical strength, reistance to abrasion and to erosion when in contact with molten masses. For this purpose two base clays were prepared consisting of :—

A.	Clay	...	70%
	Grog	...	30% and
B.	Clay	...	80%
	Grog	...	20%

The grog was the fireclay, briquetted, burnt to about 1300° C., ground and hand graded.

The final composition of the batches is shown in the following table :—

	A1.	A2.	A3.	A4.	A5.	B1.	B2.	B3.	B4.	B5.
Fireclay ...	55.10	49.00	42.90	36.70	30.60	56.00	49.00	42.00	35.00	28.00
Ball clay ...	7.90	7.00	6.10	5.30	4.40	8.00	7.00	6.00	5.00	4.00
Grog— 8+20	8.10	7.20	6.30	5.40	4.50	4.80	4.20	3.60	3.00	2.40
—20+30	8.10	7.20	6.30	5.40	4.50	4.80	4.20	3.60	3.00	2.40
—30+40	8.10	7.20	6.30	5.40	4.50	4.80	4.20	3.60	3.00	2.40
—40	2.70	2.40	2.10	1.80	1.50	1.60	1.40	1.20	1.00	0.80
Silica ...	10.00	20.00	30.00	40.00	50.00	20.00	30.00	40.00	50.00	60.00

A grading analysis of the silica showed the following result :—

—120+180	...	15%
—180+200	...	35%
—200	...	50%

The grog and silica were mixed dry, then the fireclay was incorporated and, finally, the ball clay slip was added, and the mixtures were allowed to sour for three months.

While these stages of the work were in progress it was conclusively proved that many of the laminations found in tank blocks were due to the method of rubbing up, and consequently

it was determined to mould these blocks by ramming. Hand and pneumatic methods were tried, with various shaped tools, the results being checked by cutting up the blocks as soon as rammed and examining for flaws. Eventually a combination was found which gave a good block in a reasonable time, and this method was adopted for all the blocks.

A modified form of humidity drying was attempted, but the only building available for the purpose was rather unsuitable, and several blocks were spoiled in the process.

The blocks were set in concentric rings in the upper part of a circular down-draft kiln, Watkins Recorders and Seger Cones being distributed at intervals.

The firing curve followed was considerably shorter than that usually adopted for this type of ware, the time occupied being eighteen days, whereas the usual period is from five to eleven weeks. Pyrometer elements were fitted about 12-in. below the crown and 4-in. through the base of the wicket; unfortunately, one of these elements broke down at a critical period and a complete record of the firing was not obtained. From the pyroscopes provided it would appear that a temperature of at least 1400° C. was obtained.

When the kiln was drawn it was seen that most of the blocks were ashed or very highly glazed, in some instances to a depth of as much as 5 mm. This was accompanied by an increase in alkali content in the outer portions, as shown in the following table :—

Determination of Alkalies in B2.

	Inside.	Outside.
K_2O ...	0.94% ...	1.80%
Na_2O ...	0.50% ...	1.24%

All the blocks examined were much denser and finer than the average tank block and had excellent cohesion between the grog particles and the clay. These features were maintained right to the centre of the blocks. In order to expose the test pieces

to exceptional conditions a sand-blast apparatus was used. This operated at a pressure of 8-lbs. per square inch, the tip of the nozzle being 7-in. from the top of the specimen. This treatment still further emphasised the extreme compactness of the ware.

The results of other tests are shown in the following tables :—

No.	Refractory Test.	Porosity.	Specific Gravity. True.	Specific Gravity. Apparent.
A1 ...	Cone 28 ...	20.00% ...	2.53 ...	2.02
A2 ...	„ 20-26 ...	22.05% ...	2.54 ...	1.98
A3 ...	„ 19 ...	23.30% ...	2.53 ...	1.94
A4 ...	„ 20 ...	24.30% ...	2.47 ...	1.87
A5 ...	„ 27-28 ...	26.60% ...	2.48 ...	1.82

No.	Refractory Test.	Refractories under 50 lbs. per sq. in.	Porosity.	Specific Gravity. True	Specific Gravity. Apparent
B1 ...	Cone 20-26 ...	Cone 17 ...	22.40% ...	2.58 ...	1.95
B2 ...	„ 19-20 ...	„ 14-15 ...	24.00% ...	2.50 ...	1.90
B3 ...	„ 19-20 ...	„ 17 ...	25.30% ...	2.49 ...	1.86
B4 ...	„ 19 ...	„ 17 ...	23.70% ...	2.41 ...	1.84
B5 ...	„ 20-26 ...	„ 16-17 ...	23.70% ...	2.41 ...	1.84

For testing resistance to fluxes, corrosion batches were filled into rectangular frames which had been cemented to the blocks, and these were passed through an industrial kiln. The batch corroded the cement and spread over the surface of the blocks without corroding them appreciably. The batches used had the compositions shown below :—

No. 1.		No. 2.		No. 3	
Flint Glass ...		Flint Glass...	70	Litharge ...	43.5
		Cryolite ...	20	Soda Ash ...	39.0
		Fluor ...	5	Iron Oxide ...	4.5
		Soda Sulphate	5	Soda Fluo-silicate	13.0

To test the solubility still further, glass batches of the following compositions were prepared.

	No. 1.	No. 2.	No. 3.	No. 4.
Sand ...	1000 ...	1000 ...	1000 ...	1000
Salt Cake ...	490 ...	— ...	— ...	—
Soda Ash ...	— ...	50 ...	450 ...	350
Potash ...	— ...	100 ...	— ...	—
Lime ...	200 ...	— ...	220 ...	25
Red Lead ...	— ...	600 ...	— ...	—
Cryolite ...	— ...	— ...	— ...	75
Fluor ...	— ...	— ...	— ...	200

Portions of A1, A3, B3 and B5 together with cubes from two commercial tank blocks, were immersed in each batch, heated up to 1500° C., and maintained there for about six hours. The fluoride batch destroyed all the specimens. Owing to failure of the crucible the salt-cake batch gave no conclusive results, but A3 and B5 showed less signs of attack than the others. In the lead glass the commercial blocks failed entirely, A1 was greatly reduced in size, A3 and B3 were reduced about 60 per cent. and were very rounded, while B5 lost about 50 per cent. and maintained fairly sharp edges. In the soda ash batch A1 lost about 25 per cent., A3 and B3 rather less, while B5 showed only a trace of rounding. Some of these results are contrary to general experience and no conclusions should be drawn until we have the results of the further experiments now proceeding.

Four sets of blocks were sent to various works to be floated in tanks. Two of the tanks went out before the blocks could be put in, one ran for much longer than was anticipated and the blocks disappeared entirely. Consequently, only one set of data is available and this is rather inconclusive. The blocks, including four commercial blocks, were brought up in a pot arch, reaching a dull red heat in twelve hours. They were introduced through the dog house and pushed down to the bridge. Four months later six fragments were recovered, and the only means of identifying them was by chemical analysis. The two largest fragments agreed together very closely, and fairly well with one

make of commercial block floated. Of the remainder, only one small fragment corresponded to any of the blocks floated, and it is apparently B3 as shown by the following comparison :—

		B3		Floater.
SiO_2	...	80%	...	80.40%
Al_2O_3	...	15%	...	14.80%
TiO_2	...	0.8%	...	0.95%

Unfortunately, owing to the fact that most of the experimental blocks were badly cracked, the sizes of the fragments recovered gives no clue to their relative solubilities.

V. Report

upon the Manufacture of Tank Blocks for an Experimental Furnace carried out at Stourbridge. January—April, 1923.

By the Staff of the Glass Research Association.

Abstract: Description of raw materials, composition and method of manufacture of blocks for an experimental furnace. Important points for future investigation were raised by (a) the presence of free hydrogen in the flue gases during the greater part of the burn, and (b) the pronounced effect of atmospheric changes upon the control of temperature and kiln conditions generally.

THE objects of the work about to be described are twofold: (1) To investigate (a) the utilization of natural sillimanite as a refractory material, and (b) the effect of free silica in resisting erosion and solution. (2) To try out modifications in the various methods of manufacture suggested mainly by observations made during the previous year and summarized in the previous article. These modifications are (a) using the minimum amount of raw clay to produce a workable mixture, (b) pneumatic ramming in place of " rubbing up " with a view to avoiding laminations, (c) kiln-drying (on a few specimens only), and (d) a greatly shortened firing curve.

I. MATERIALS USED.

(1) "*O.M.*" *Selected Fireclay.*

THIS clay occurs in a very narrow, rather irregular seam

and cannot be picked out in the mine. Its composition is as follows :—

SiO_2	64.30
TiO_2	1.32
Al_2O_3	21.34
Fe_2O_3	1.88
CaO	0.51
MgO	0.34
K_2O	1.02
Na_2O	0.84
Loss	8.90
	100.45 (Dr. J. W. Mellor)

The mixed clay and offal is tipped over the edge of a large dump, the fireclay is hand picked and stacked in small heaps where it is allowed to weather for about a month. The raw clay was ground, pugged and re-ground.

(2) " *D* " *Fireclay.*

This clay is rather aluminous and short, but after four or five puggings it develops a very good workability. Analysis gives the following result :—

SiO_2	49.70
TiO_2	1.00
Al_2O_3	33.90
Fe_2O_3	2.30
CaO	0.20
MgO	0.30
Alk (as Na_2O)	1.20
Loss	12.00
	100.50

It is separated from offal in the mine, and allowed to weather for about a week, after which time it is completely disintegrated. The raw clay was ground, pugged twice and re-ground.

(3) *Ball Clay.*

The clay used was of the composition shown below :—

SiO_2	50.25
TiO_2	0.91
Al_2O_3	33.26
Fe_2O_3	1.62
CaO	0.12
MgO	0.63
K_2O	2.66
Na_2O	0.50
Loss	9.79
	99.74 (Dr. J. W. Mellor)

The clay occurs in a seam about 10′ thick and is obtained from a shallow mine.

For batches A and B the weighed quantity of clay was slipped by hand in a tub while the blunger was under repair. For the other batches the clay was blunged and the slop weight taken every day.

(4) *Grog.*

Batches A and B were compounded of "O.M." selected clay burnt in lumps to about 1,220°C and graded by hand. Other batches contained "D" clay briquetted and burnt twice as a kiln filling for tank blocks to a temperature of 1,350°C. The following is grading analyses of this grog :—

+ 8s	1.3%
— 8 + 20	30.9%
—20 + 30	17.9%
—30 + 40	14.4%
—40	35.2%
	99.7%

Before mixing, the coarsest particles were screened out, and the grog actually used had the following composition :—

— 8 + 20	31.3%
—20 + 30	18.1%
—30 + 40	14.6%
—40	35.8%
	99.8%

(5) *Silica.*

A quartzite rock crushed to—120 mesh was used. The analysis is as follows :—

SiO_2	95.00
Fe_2O_3	0.23
Al_2O_3	2.83
TiO_2	0.14
CaO	0.15
MgO	0.20
Na_2O	0.04
K_2O	0.39
Loss	0.84
	99.82

(6) *Sillimanite.*

This was the natural mineral crushed to various gradings The composition is as follows :—

Al_2O_3	58.48	
SiO_2	35.23	
Fe_2O_3	2.50	
TiO_2	2.40	
CaO	n.d.	
MgO	n.d.	
Loss	1.29	
	99.90	(Messrs. G. T. Holloway & Co.)

II. BATCH FORMULÆ.

The batch formulæ adopted are given below. Each batch was divided into an X and a Y series compounded of " O.M." selected and " D " fireclays respectively.

A 4.	Fireclay	36.70	**A 5.**	Fireclay	30.60
	Ball Clay	5.30		Ball Clay	4.40
	Grog — 8+20 ...	5.40		Grog — 8+20 ...	4.50
	—20+30 ...	5.40		—20+30 ...	4.50
	—30+40 ...	5.40		—30+40 ...	4.50
	—40 ...	1.80		—40 ...	1.50
	Silica	40.00		Silica	50.00
		100.00			100.00

B 3.	Fireclay ...	42.00
	Ball Clay ...	6.00
	Grog — 8+20	3.60
	—20+30	3.60
	—30+40	3.60
	—40	1.20
	Silica ...	40.00
		100.00

B 4.	Fireclay ...	35.00
	Ball Clay ...	5.00
	Grog — 8+20	3.00
	—20+30	3.00
	—30+40	3.00
	—40	1.00
	Silica ...	50.00
		100.00

A 4a.	Fireclay ...	36.70
	Ball Clay ...	5.30
	Grog ("D")	18.00
	Silica ...	40.00
		100.00

A 5a.	Fireclay ...	30.60
	Ball Clay ...	4.40
	Grog ("D")	15.00
	Silica ...	50.00
		100.00

B 3a.	Fireclay ...	42.00
	Ball Clay ...	6.00
	Grog ("D")	12.00
	Silica ...	40.00
		100.00

B 4a.	Fireclay ...	35.00
	Ball Clay ...	5.00
	Grog ("D")	10.00
	Silica ...	50.00
		100.00

C 1.	Fireclay ...	20
	Ball Clay ...	10
	Grog — 8 ...	30
	Silica ...	40

S 2.	Firelay ...	25
	Sillimanite — 10	70
	Silica	5

C 2.	Fireclay ...	20
	Ball Clay ...	10
	Grog — 8 ...	50
	Silica ...	20

S 3.	Fireclay ...	30
	Sillimanite 30 — 36	70

D 1.	Fireclay ...	35
	Grog — 8 ...	50
	Silica ...	20

S 4.	Fireclay ...	35
	Sillimanite — 30	35
	Silica ...	30

S 1.	Fireclay ...	25
	Sillimanite — 30	70
	Silica ...	5

S 5.	Fireclay ...	35
	Sillimanite fines	65

III. COMPOUNDING.

The materials were hand mixed and soured for a week, during which time each batch had at least three puggings. Full details of this treatment, together with any peculiarities in behaviour are given in Table I.

FIG. 1.

FIG. 2.

IV. FORMING, DRYING AND DRESSING.

All the blocks were moulded by pneumatic ramming. The 12″ mould was lined with canvas, and the 24″ mould with oil. Two ramming tools were used. One was a blunt-nosed rammer of about 3″ × $\frac{3}{4}$″, and the other was a treble-nosed ram, each nose being about $2\frac{3}{4}$″ × $\frac{1}{2}$″. The blocks rammed with each tool are shown in Table I.

Drying was carried out on a very slightly warmed floor in the moulding room, and during the last three days, the blocks were slicked to shape.

Trial shapes, consisting of 9″ × 4″ × 3″ briquettes, 4″ cubes and 10″ × 2″ × 2″ bars were hand moulded.

V. SETTING.

The blocks were all placed at the top of the kiln, the bottom of the blocks being just above the level of the bag wall.

Seger cones were set in the wicket and Watkins Recorders 31—39 on every block and at various places throughout the kiln.

The trial pieces were boxed in just in front of the wicket, which was built up to allow pieces to be withdrawn easily during the progress of the burn. Photographs of the setting are shown in figs. 1 and 2. Two pyrometer elements were fitted, one 5′ in through the wicket and 9″ above the floor; the other 2′ in through a crown hole. The stack was fitted with a Draught Gauge and a CO_2 recorder. The latter did not work satisfactorily, and the results are discussed in a subsequent section.

VI. FIRING.

As will be seen from the following details the firing curve adopted was very rapid.

20°— 110°C	...	...	at 3° per hour.
110°— 120°C	...	...	24 hours.
120°— 440°C	...	...	at 5° per hour.
440°— 450°C	...	...	24 hours.
450°— 510°C	...	...	at 3° per hour.
510°— 600°C	...	...	at 10° ,,
600°— 855°C	...	...	at 15° ,,
855°—1400°C	...	...	at 20° ,,
1400°C	...	...	48 hours.

Details of the firing curve are shown on the accompanying chart.

A complete log of the firing is given in the appendix.

During the previous burn it was noticed that towards the end of the firing the supply of air was very restricted. While the mixing was in progress a trial hole 6″ square was cut out over one fire hole of the kiln and it was found to effect a pronounced improvement in the quality of the ware, consequently similar holes were cut over all the grates of the kiln used for this burn.

As can be seen from pyrometer curves (Fig. 6) there were considerable fluctuations in the temperature for the first two days. This was remedied as soon as the stokers were trained to observe the recorder at frequent intervals and to drop entirely their old methods of firing. (It should, perhaps, be mentioned here that the usual time for burning tank blocks at this works is five weeks as against the ten days required by our firing curve.) An effort was made to reduce the lag between the top and bottom temperatures, but the results leave much to be desired ; this is due in part to the design of the grates.

The first trial draw was taken at 250°C and the bricks were found to have an average water content of 0.18%. Further draws were taken at various stages and these were all quite satisfactory. The texture throughout was very good and the bricks were well knit at as low a temperature as 600°C.

VII. ACTION OF CO_2 RECORDER.

At a trial run this was found to be working well, but when our burn was made no record was obtained ; the meter showed some signs of flooding and distortion of the vulcanite ring and a new meter was obtained, but still no record was given. The galvanometer circuit of the meter was tested and found good ; when the meter was breathed upon the recorder immediately showed a reading of 5% CO_2 ; the aspirator was tested and pressure of at least 3″ of water was obtained ; the soot filter was also dried out and re-sealed and found to be in good working order. The condensation tube was then cleaned out and a

collecting tube sealed into it, the other end being put into a fire ; this resulted in a reading of 6% CO_2. The only remaining part of the installation, viz., the conduit from the flue to the meter, was carefully inspected (all the joints being re-sealed), but no fault was found. This left free hydrogen as the only possible explanation.

Previously the recorder had always been run with an iron collecting tube in the flue, but as all the flue tubes were burnt off during our last run a silica tube was substituted. This was replaced by an iron tube and a reading of between 8 and 9% was obtained within a few moments. As a check the silica tube was replaced and the readings promptly dropped to zero. Small wads of cupric oxide were then introduced into the tube and positive readings were obtained ; further, there was a heavy condensation of moisture in the tube which previously had been quite dry.

The foregoing tests indicate the presence of free hydrogen in flue gases and there are three possible sources for it :—

(1) *It may be produced by interaction of the fuel gases*, but this seems rather doubtful. The fuel was fairly dry, the fires were open with ample air above and below and with the secondary air holes at their maximum ; also the recorder showed a content of about 12.5% CO_2 indicating an ample excess of air, further, the temperature at the top of the kiln was 680°, i.e., 130° above the ignition temperature of hydrogen. Taking all the circumstances into consideration it seems unlikely that the free hydrogen was derived directly from the fuel.

(2) *As the result of interaction in the clay.* Although the top temperature was well above the ignition temperature of hydrogen the bottom temperature was 70° below it and consequently any hydrogen evolved from the lower courses of the kiln setting would have a chance of reaching the stack uncombined.

(3) *By the action of the flue gases on the silica tube.* The fact that not the slightest sign of disintegration was noticed on the satiny surface of the tube is strongly against this explanation.

The question of the origin of this hydrogen is of considerable importance and it is proposed, if circumstances permit, to make an exhaustive investigation of the problem during the next few burns. It is intended to make analyses of the kiln gases at three or four selected spots throughout the run and also to introduce collecting tubes into various parts of a few blocks and analyse the gases produced in these.

VIII. SPECIAL FEATURES OF THE BURN.

Several interesting features were observed when the kiln was drawn.

In the first place, owing to the excessive ash in the fuel, there was a considerable amount of glazing and consequent spalling. All the glazed blocks were badly cracked, not only at the corners, but all over, and the cracks were not confined to the surface, but extended all the way through the blocks. A very few of these fissures showed signs of commencing as drying cracks but the great majority gave no indication of their origin. The blocks most affected in this way belonged to the A and B series; of the other clay and silica blocks, series C was less affected and series D showed practically no glazing. The last series contained no ball-clay, and this may afford a partial explanation of the phenomenon. A very remarkable feature of the glazing is the fact that the 12″ cubes were much more glazed than 24″ × 12″ × 12″ blocks of identical composition. The moulds for the small cubes were lined with cloth, and those for the large blocks with oil, but as all the surfaces were scraped off, it is difficult to see how the lining affords any explanation. It may be thought that the process of scraping brought about concentration of very fine, easily fused particles on the surface. This might apply in the case of a damp block, but the small blocks were all moulded

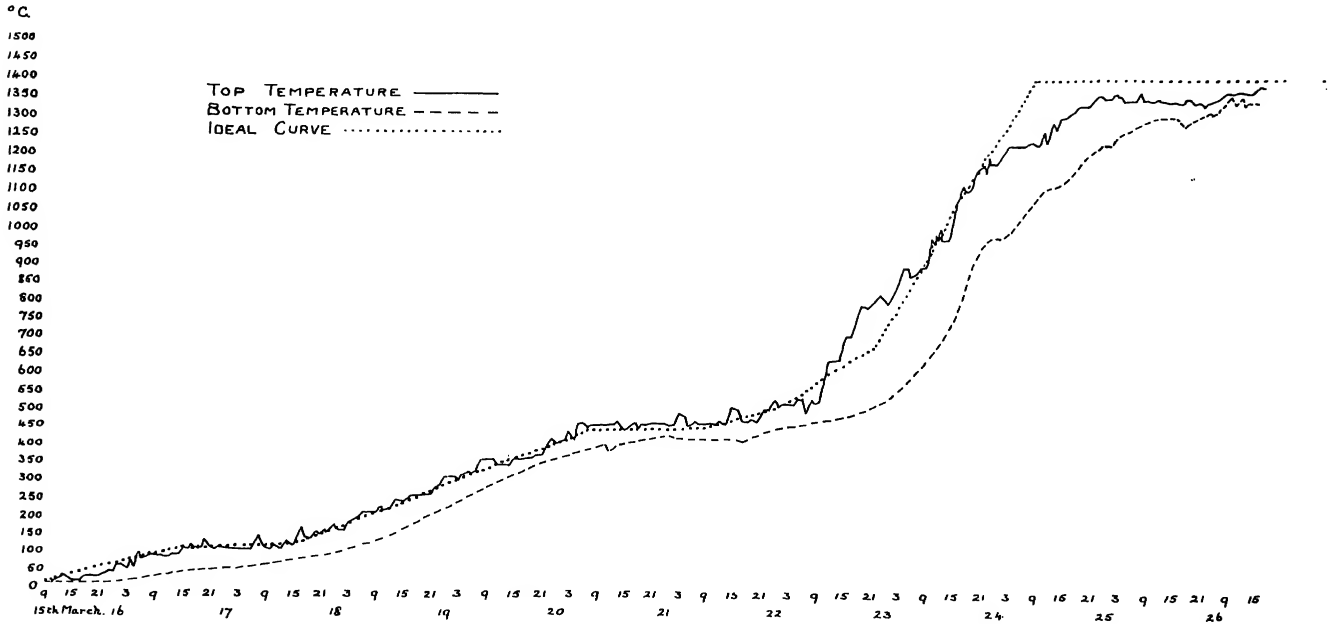

°C.
TOP TEMPERATURE
BOTTOM TEMPERATURE
IDEAL CURVE
15th March. 16
17
18
19
20
21
22
23
24
25
26

FIG. 6.

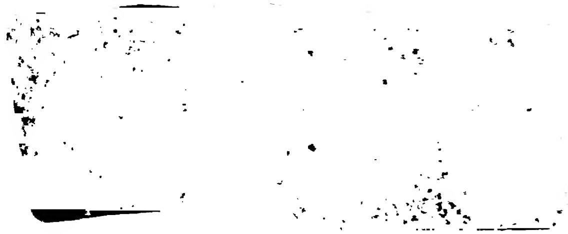


FIG. 3.

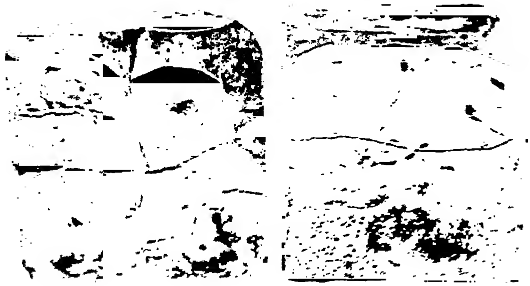


FIG. 4.

FIG. 5.

considerably before the large ones and were quite dry at the time of dressing.

As previously mentioned, a Watkins recorder was placed on each block, and these were covered by a semi-circular boiler brick, and although these bricks had a thick coating of ash they were not glazed. Also, the sillimanite blocks, almost without exception, appear to have repelled the ash ; at any rate, very few of them have even a rough coating. A very striking instance of this is illustrated in fig. 5, where it will be seen that the covering boiler brick has a pronounced ash coating, whereas the sillimanite block upon which it rests shows no sign of this. It is interesting to note that in the kiln this block was adjacent to the block shown on the left in fig. 4, which is very highly glazed.

In view of the difficulties attending the drying of large blocks it was decided to introduce a few damp blocks into the kiln. Four such blocks were prepared, three of them being " black-hard " and one semi-plastic, at the time of setting. Although the steepness of the curve was against the experiment being successful, the condition of these blocks was very satisfactory. Only one of them (the semi-plastic block) was at all cracked, and even that no more than some of the blocks which had been dried white-hard. It is true that with a whole kiln setting of black-hard material, the results may not be so satisfactory, but the success of this trial makes it well worth while to investigate the possibilities of kiln drying, and it is proposed to carry out further experiments in this direction in future burns.

It is worth noting that with the exception of the boiler bricks practically the whole of the ordinary clay products with which the kiln was filled was badly black-cored ; an illustration of this is attached (fig. 3). Apart from the method of moulding the only way in which this material as a whole differs from our blocks (except the " S " series) is in the high proportion of raw clay in their composition ; in our blocks the raw clay averages about 35% whereas the ordinary ware contains 50% or more.

The temperature distribution in the kiln, as shown by the Watkins recorders, was remarkably uniform.

IX. SHRINKAGE.

The following shrinkages after firing were measured on 10″ bars.

A 4 a X	2.9 %	D 1 X	4.81%
A 4 a Y	3.3 %	D 1 Y	4.75%
A 5 a X	2.3 %	S 1 X	4.92%
A 5 a Y	0.0 %	S 1 Y	2.9 %
B 3 a X	3.21%	S 2 X	3.08%
B 3 a Y	4.25%	S 2 Y	2.45%
B 4 a X	1.25%	S 3 X	2.80%
B 4 a Y	1.40%	S 4 X	5.60%
C 1 X	0.62%	S 4 Y	3.12%
C 1 Y	0.20%	S 5 X	2.96%
C 2 X	4.63%	S 5 Y	3.12%
C 2 Y	4.40%		

It will be observed that in the majority of instances the "Y" series (compounded of "D" clay) show less shrinkage than the corresponding mixtures of the "X" series, compounded of selected "O.M." clay.

APPENDIX.

Firing Log.

14.3.23	8 p.m.	First fire commenced. Secondary air 1/3 open.
15.3.23	8 a.m.	Second fire commenced.
	1 p.m.	Third fire commenced.
16.3.23	8 p.m.	Fourth fire commenced.
	11 a.m.	Fifth fire commenced.
	12 noon.	With a view to pulling up the bottom temperature a stack damper was completely removed and a straw fire put in; which had a very slight effect.
	4.15 p.m.	Stack fire re-lighted and maintained until the next day.
	5 p.m.	Grates not in use were covered to prevent ingress of cold air.
	7 p.m.	Stack fire increased followed by a slight rise in bottom temperature.
	7.45 p.m.	Two fires slightly damped owing to sudden increase in top temperature.

	10 p.m.	Wind became more constant and it was possible to obtain a better curve. Stack fire increased. Considerable volume of steam leaving the stack.
17.3.23	1 a.m.	Slight increase in bottom temperature possibly due to increased stack fire at 10 o'clock.
	6 a.m.	Considerably less steam issuing from stack.
	8 a.m.	Evolution of steam ceased.
	11.45 a.m.	Fires slightly damped.
	1 p.m.	Bottom temperature fluctuating violently.
	1.30 p.m.	Stack fire withdrawn.
	2.45 p.m.	Bottom thermo-couple tube re-sealed, stopping fluctuations in bottom temperature.
	3.30 p.m.	Bottom temperature still lagging greatly, so fires raked out and pushed down towards bag wall.
	5.30 p.m.	Two new fires started under the bars in an attempt to bring up the bottom temperature.
	6.45 p.m.	Under-bar fires commenced in remaining grates.
	10.30 p.m.	One under-fire put on bars.
18.3.23	0.5 a.m.	Another under fire put on bars.
	8.30 a.m.	Two remaining under-fires increased.
	9.30 a.m.	These fires still further increased.
	10 a.m.	Appreciable increase in bottom temperature.
	12.30 p.m.	Back of grates cleaned out; new trial claw tested, giving rise to fluctuations in bottom temperature.
	3 p.m.	Stack fire lighted.
	5 p.m.	Stack fire extinguished as it had no appreciable effect upon the bottom temperature.
	6 p.m.	Remaining under-fires put on bars.
	7.30 p.m.	Stack fire again lighted.
	9.30 p.m.	Stack fire extinguished.

19.3.23	6 a.m.	The wind, which from the commencement of the burn had maintained a constant easterly direction, showed a tendency to veer towards the north resulting in unequal burning of the fires; this probably accounts for the sudden jump in top temperature.
	2 p.m.	Wind fluctuations very pronounced rendering it exceedingly difficult to obtain a good firing curve.
20.3.23	4 a.m.	Wind very gusty and changeable causing big fluctuations in the curve.
	11.50 a.m.	Trial pieces drawn.
21.3.23	2.15 a.m.	Rain and high wind followed by increase in top temperature.
	3.30 a.m.	Temperature brought back to curve by careful damping of two fires.
	4.30 p.m.	C2X and B4aX drawn as trials.
22.3.23	4.20 a.m.	Change of wind towards the north resulting in sudden increase of top temperature.
	5.30 a.m.	Temperature brought back to curve by judicious damping.
23.3.23.	10.30-12.30 a.m.	Trials with CO_2 apparatus (see full report.)
	3.10 p.m.	As stack fires did not succeed in bringing up the bottom temperature, the effect of checking velocity by half closing the stack damper was tried.
	4.30 p.m.	No increase in bottom temperature so the damper was fully opened.
	7 p.m.	The CO_2 recorder which had been rising gradually since 2 p.m. showed a reading of 18%
	12 midnt.	CO_2 reading over 22%; secondary air holes were two-thirds opened and the fires were raked constantly and kept as low down on the bars as possible to allow a better access of air but without result.
24.3.23	10.15 a.m.	Platinum thermo-element substituted for base metal couple in wicket.

	11.15 a.m.	Secondary air holes completely opened.
24.3.23	4.15 p.m.	C1Y and B5aX drawn as trials.
	11.15 p.m.	Top temperature rather low; secondary air holes 2/3 closed.
	11.20 p.m.	Top temperature slightly increased; CO_2 risen from 16% to 20%.
	11.45 p.m.	Stack damper one quarter closed, followed by slight increase in temperature.
25.3.23	0.5 a.m.	Secondary air holes 5/6 closed.
	3 a.m.	Good coal ran out; impossible to keep good curves with slack supplied.
	5 a.m.	Stack damper half closed.
	10.35 a.m.	Back pressure in kiln, so stack damper fully opened.
	10.45 a.m.	Stack damper half closed.
	11.10 a.m.	Stack damper fully opened.
	11.50 a.m.	Secondary air holes half closed.
	12.45 p.m.	Secondary air holes two-thirds opened.
	1 p.m.	Cone 7 down.
	3 p.m.	New coal arrived.
	4 p.m.	Appreciable improvement in curves. S5X drawn as trial.
	8.30 p.m.	Back pressure in kiln, shown by flames rushing out of all secondary air holes and wicket stopper.
	11 p.m.	Strong air current in through all air holes. Cone 12 down.
26.3.23	2.45 a.m.	CO_2 meter flooded; recorder disconnected. Cone 14 apparently commencing to sag, so temperature kept at reading shown by bottom thermocouple.
	4 a.m.	Cone 15 down.
	12.50 p.m.	D1X and S2X drawn as trial.
27.3.23	2 a.m.	Violent fluctuations in bottom temperature; these were seen later to be due to collapse of bag wall.
	10.50 a.m.	Bag wall badly collapsed. Trials were drawn and it was seen that the setting had collapsed.
	11 a.m.	Firing back commenced.

TABLE I.

Batch.	Mixed.	Pugged.			Rammed.	Tool No.
A 4 X	30.1	30.1	31.1 (2)		1.2	1
A 4 Y	30.1	30.1	31.1 (7)	7.2	5.2 7.2	1 1
A 5 X	31.1	31.1	1.2	2.2	2.2	1
A 5 Y	2.2	2.2 (2)	3.2		3.2 5.2	1 1
B 3 X	5.2	5.2	6.2 (2)	7.2	5.2 12.2	1 1
B 3 Y	2.2	2.2	3.2	9.2	9.2	1
B 4 X	5.2	5.2	6.2 (4)	9.2	12.2	1
B 4 Y	5.2	5.2	8.2	12.2	14 2	1
A 4a X	8.2	8.2	15.2 (7)	17.2	17.2	1
A 4a Y	9.2	9.2	12.2 (2)	3.3	3.3	1
A 5a X	21.2	21.2	26.2	3.3	3.3	2
A 5a Y	18.2	18.2	21.2	26.2	26.2	2
B 3a X	18.2	18.2	21.2	26.2	26.2	2
B 3a Y	25.2	25.2	25.2	3.3	5.3	2
B 4a X	27.2	27.2	1.3	2.3	4.3	1
B 4a Y	28.2	1.3	1.3	3.3	5.3	2
C 1 X	8.2	8.2	16.2	17.2	17.2	1
C 1 Y	9.2	12.2	16.2	17.2	17.2	2
C 2 X	9.2	13.2	15.2	16.2	16.2	1
C 2 Y	12.2	12.2	13.2	20.2	20.2	2
D 1 X	15.2	16.2	17.2	23.2	23.2	2
D 1 Y	15.2	16.2	17.2	23.2	3.3	1
S 1 X	6.2	8.2	15.2	15.2	15.2	2
S 1 Y*	14.2	16.2	17.2	21.2	21.2	2
S 2 X	17.2	17.2	18.2	24.2	24.2	2
S 2 Y	17.2	17.2	18.2	24.2	24.2	2
S 3 X*	15.2	15.2	21.2	22.2	22.2	2
S 4 X	14.2	14.2 (2)	18.2		21.2	2
S 4 Y	15.2	15.2	15.2	22.2	22.2	2
S 5 X†	16.2	16.2	18.2	24.2 (6)	24.2	2
S 5 Y†	16.2	16.2	18.2	24.2 (4)	24.2	2

* These mixtures required very careful adjustment of water; the slimy condition of S 5 was not noticed (owing probably to the coarser grain), but a partial separation occurred in the pug, the coarser particles clogging the perforations and leaving the lower blade churning through a thick mud.

† These batches were very troublesome to work, as at a certain stage in mixing, the addition of a very slight amount of water made the whole mass slimy, whereas the addition of a little of the dry mixture rendered the whole mass too sandy to go through the pug.

GLASS RESEARCH ASSOCIATION BULLETIN.

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CONFIDENTIAL TO
THE MEMBERS OF
THE GLASS
RESEARCH
ASSOCIATION.

LONDON
GLASS RESEARCH ASSOCIATION,
50, Bedford Square, W.C. 1.

NOTE.

The Council of the Association does not hold itself responsible for the opinions expressed by the contributors of the various articles.

Contents.

Foreword.

IN addressing Members of the Association at a General Meeting on November 15th, 1921, I made the following remarks :—" I have made numerous inspections at various plants and in each case have inquired concerning the problems with which they have had to deal and which effect the greatest loss in value of investment, and have found that the major losses may be attributed to the following causes :—

(1) Failure of clay materials.
(2) Defective organisation.
(3) Defective technique.
(4) Faulty design in equipment.
(5) Faulty composition of glass."

My desire for the prosecution of a study of the physiological and psychological conditions existing in the factories of many of our Members can therefore be appreciated and the report which follows has confirmed my understanding and belief that the organisation of the employees, the co-ordination of the steps in the processes of manufacture of any given article, the correlation of the work performed, the selection of individuals performing such work, and the time period of such performance are of paramount importance to successful and perfect organisation.

The Report of Mr. Farmer and his colleagues substantiates the need of this selection and organisation and he makes particular reference to this when he says in paragraph 2, page 11 :—" also it illustrates the difference between the fatigue due to heavy muscular exercise and fatigue due to the constant repetition of a group of intricately co-ordinated movements involving conscious supervision."

The Report is valuable because it brings before manufacturers the importance of the human factor in the operation of

their plants. Manufacturers are to-day considering the installation of machines and various appliances in their glasshouses, and there is a tendency to overlook that careful and efficient organisation of the human element which goes to give success to the endeavours of the factory. Without carefully organised and co-ordinated human activities the best endeavours of the factory management will be futile.

Many Members no doubt will consider that much of the data contained in this Report does not relate to or has no bearing upon their situation. I would, however, urge every manufacturer to read carefully this Report and extract therefrom only those points which may appear to him to be applicable, and if he will then discuss these points with his factory superintendent and foremen, I am quite sure that many useful and beneficial points will arise during such discussions which will inform him of conditions which hitherto he may not have appreciated.

I regret to state that from my enquiry in the trade I have ascertained that reports of this character are too often casually read or possibly only glanced at and, because of the curves and figures, certain manufacturers are too prone to lay them aside without full and serious consideration. I suggest that this Report be put into the hands of the factory superintendent and foremen for their perusal, with the request that they offer criticisms and a discussion of the subjects therein. Such a method of treating the Report will bring up a consideration of various points. For example, why should the morning shift be less efficient than the afternoon shift; why should the night shift be less efficient than the afternoon shift; why should the efficiency in the making of small bottles be lower than the efficiency in the making of large bottles, even in spite of the fact, as we all know, the larger the ware the greater number lost because of imperfect making conditions.

From the curves and records shown it would appear (and I am quite sure that it is correct) that much of the profits in the making of ordinary bottles or simple forms of glassware are consumed in the changing of the type of ware made by any one chair, for, as will be seen by the records, it takes approximately

ten weeks for one to become accustomed to a complete change in gathering and forming ware having different shape and weight, and this strongly emphasizes the fact that manufacturers should make even greater efforts than in the past to obtain contracts for quantities of ware that will keep their workmen employed upon a specific type for long and continuous periods. The efficiency in the manufacture should reflect in the ultimate price and should be a matter of mutual benefit, both to the consumer and manufacturer.

The investigation which is described in the following pages was carried out by officers of the Industrial Fatigue Research Board, working in conjunction with the Glass Research Association and the investigations were controlled by a Joint Committee consisting of nominees of the Industrial Fatigue Research Board and the Glass Research Association.

The investigation was financed by both bodies, the Industrial Fatigue Research Board bearing approximately two-thirds of the cost.

This Report will subsequently be issued to the general public by the Industrial Fatigue Research Board.

R. L. F.

A Preliminary Investigation in the Glass Trade dealing with the Optimum Spell of Work.

By E. Farmer, M.A. (assisted by R. S. Brooke, M.A., M.C. and E. G. Chambers, B.A.).

Introduction.

THE Glass Industry is a peculiarly difficult one in which to carry out an inquiry concerning the human side of manufacture. So many different articles are manufactured, the methods of manufacture and the length of hours worked vary so much that it is hard to obtain reliable data which would yield comparisons useful to the industry as a whole. After visits to a considerable number of firms manufacturing various forms of glassware in different parts of the country, it was decided to pay special attention to the problems of the optimum length of the working spell. This decision was arrived at—

(1) Because in the Yorkshire district a change had recently been made from a ten hour to an eight-hour shift, and it was thought that reliable data regarding this change might be obtainable from certain firms, which although it could not form a basis of comparison between various firms and therefore various methods, would nevertheless be available for comparison between different practices employed at different times by the same firm. It was felt that if such an inquiry showed the presence of some general principle affecting the problem of the optimum length of the working spell, it might be applicable to other districts and so be of general use.

(2) Because differences of opinion existed in the trade concerning the advisability of the long and short shift methods and therefore any light which could be thrown on their relative efficiency by an outside observer might be of use to those who were endeavouring to arrange for the most economic working conditions.

(3) Because if any conclusions could be arrived at under the comparatively uniform conditions existing in Yorkshire, concerning the central problem of human fatigue—the only factor common to all glass works—deductions might be drawn throwing light on the advisability of other ways of arranging the working day.

General Description of Processes.

The Glass industry in Yorkshire is mainly concerned with the manufacture of bottles, and so one of the many variables affecting this inquiry was removed. The processes of manufacture fall into three categories :—

(1) Hand made.

(2) Semi-automatic.

(3) Automatic.

Hand-made Processes.

1. In the hand-made method two slightly different processes are in use, both of which have existed almost unchanged for generations.

(i) In the first of these the workers, three in number, are called " flint hands." Two of these are blowers, and the third is the maker. Each blower gathers the molten metal on his " iron," rolls it, blows it out in the mould, and then " cuts down " or " bursts off " the bottle into a tray near the maker. The maker takes the bottle into a gadget shaped to fit it exactly, heats the neck for a time in a small furnace or " glory

hole," and then shapes the neck with a tool specially made for the purpose. The bottle is then finished, and is carried away to the annealing lehr by a boy called a "taker-in." In this process each "chair" comprises four workers.

(ii) In the alternative process the workers are called "bottle-makers." In this a "chair" consists of five workers. First there is a gatherer whose duty is simply to gather the molten metal on to an iron. The blower takes the iron from him, rolls the metal and blows it out into the mould. Next the "melter-off" takes over the iron from the blower, gives a final blow into the mould, and then "wets off" the bottle into the maker's tray. The process of "making" the bottle is different here, for the maker, after heating the neck adds a ring of molten metal to the neck before he shapes it with his tool. Finally, the "taker-in" removes the finished bottle to the lehr.

Semi-Automatic Processes.

2. In the so-called "semi-automatic" processes there is a large variety of machines in use. The bulk of these have several features in common, and differ chiefly in size and accessory mechanism. The process of making a bottle with one of these machines is as follows:—The gatherer gathers the molten metal from the tank and drops a sufficient quantity into the parison mould which is then brought in front of the blower by rotating the machine. He inverts the mould, opens it, and pats the metal with a movable platform until it has the right consistency. Then he closes the mould and turns on an air-jet which blows the bottle. Finally, the machine is rotated again to a third worker who opens the mould and removes the bottle, putting it on a tray or roller, whence the taker-in removes it to the lehr. This third man also closes the mould and lubricates it, and by the next rotation of the machine it assumes its upright position in front of the gatherer.

There is also a type of machine which more nearly approaches the fully automatic machine, the chief difference being that it has to be "fed" by hand: the remainder of the process is automatic.

Automatic Processes.

8. In the fully automatic processes the whole making of the bottle is done by machinery. The metal is gathered or fed by the machine and blown out by an air-jet, and the only human co-operation necessary is the supervision of the machine.

Methods of Investigation.

A large number of firms kindly placed their records at the disposal of the investigators, but it was only possible to make use of comparatively few of them. This was due to two main causes :—

(1) The records were kept in such a way that it was impossible to elicit the specific information required for this investigation.

(2) Owing to changes brought about by the war, some firms had not manufactured one type of bottle for a sufficiently long period to yield reliable data.

It was found that in the Yorkshire district a re-arrangement of the working day had taken place in July, 1919. Previously to this time the day had been divided into two ten-hour shifts whereas after this date it was divided into three eight-hour shifts. Workers were in all cases paid by results.

The method adopted was to select bottles which had been made for a lengthy period by the same chairs under both methods of subdividing the working day. The average output per shift during each month in the two periods was calculated, and the average hourly output per chair found. In order to make the data strictly comparable periods for comparison were chosen as far as possible comprising the same months, so as to eliminate possible effects of seasonal variation. In certain cases war and post-war periods have been compared, but it should be borne in

mind that it was always the output of the same chair which was compared, and so the possibility of a less efficient type of labour during the war period affecting the figures is removed. We were constantly informed by managers that during the war the workers were keener on producing their maximum output than after the war. If this is so it would tell against the increased hourly output which accompanied the change of shift in 1919 shown in the following tables, and had this special war incentive not been operating the increase might have been even greater than it is. In certain cases difficulty was experienced during the war in getting a regular supply of coal and raw material, and in order to guard against this interfering factor no records were used unless they were regarded by those who had kept them as being thoroughly reliable. Many records which were offered to the investigators were not used for this reason alone, and those which are presented in this report are believed to be trustworthy and as free as possible from external interfering causes. Table I. gives the comparison of the average hourly output for various types of hand-made bottles taken from the records of four firms.

Table I*. shows that in practically every case the hourly output is higher for the eight-hour shift than for the ten-hour shift. It should also be noted that there appears to be a tendency in three of the factories for the increase in hourly output to be greater with the heavier bottles than with the lighter. This is interesting, not only in view of the already known fact that the human body cannot profitably continue to do work involving heavy muscular effort for so long a period as it can continue to do work of a less arduous type; but also because it illustrates the difference between the fatigue due to heavy muscular exercise and fatigue due to the constant repetition of a group of intricately co-ordinated movements, involving conscious supervision but comparatively little muscular effort. These records seem to indicate that heavy muscular work involves a type of fatigue which can be alleviated by shortening the working spell, whereas the fatigue involved in the constant repetition of an intricate operation is not relieved by this method to the same extent.

Comparisons wherever possible were also made between the amount of spoilt work recorded during both periods, and the

* Tables and Figures are printed at the end of the Report.

results are given in Table II. from which it will be seen that there is a slight decrease in the amount of spoilt work for the smaller bottles, on which the smallest increase of output was made, and an increase in the amount of spoilt work for the heavier bottles, on which the greatest increase of output was made. From this it would appear that the increase in output is not entirely due to lessened fatigue, but is also partly accounted for by the natural desire of the workers to increase their output during the shorter hours so as to bring up their earnings to their previous standard. It should, however, be borne in mind that the standard of inspection was raised considerably in the years 1920 and 1921, when the effects of the war demand were drawing to a close and the ordinary process of competition taking its place. Moreover, it is easier to spoil a larger bottle than a smaller one, which may account in some way for the increased amount of spoilt work in the case of the heavier bottles as compared with the decreased amount of spoilt work in the case of the smaller bottles.

A third way of comparing the relative efficiency of the two methods of dividing the working day was to investigate the amount of time lost under both systems. Unfortunately, records dealing with this subject could only be obtained from one firm, and so too much reliance should not be placed upon them. These records are, however, given for what they are worth in Table III. The time lost has been divided into two classes.

(1) All absences except those extending over four consecutive weeks. (Special circumstances made it advisable not to include those absences of more than four weeks because two workers underwent operations during the earlier period for complaints entirely unconnected with their occupation, and if these absences had been included it would have made the difference betweeen the two periods appear greater than they were likely to be when these special circumstances were absent.)

(2) Absences of 2 days and under. (No absence less than a whole shift was counted, but a distinction between the long and short absences was made, since the short absences are probably the more important indications of fatigue.) It will be seen from Table III. that there is a slight decrease in the amount of time lost during the shorter shift period compared with the amount

of time lost during the longer shift period. The difference is a small one, and in order to make this conclusion definite, further evidence must be collected.

Semi-automatic.

The data obtained concerning the semi-automatic method of glass-blowing are given in Table IV., where it will be seen that there is an increase in hourly output in every case coinciding with the introduction of the shorter shift. The output for No. 3 factory only shows an increase of 5.3 per cent. compared with that of 35.5 per cent. for No. 5 factory, making the same article but with a different type of machine. This difference is probably due to the fact that in factory 3 (previous to the change in shift) a far higher standard of output had already been attained than that attained in factory 5, so that any increase in hourly output would be proportionately difficult. There can be no doubt that part of this increased output is due to a spurt on the part of the workers. This is shown in Figure 1, where a spurt immediately following the change in shifts is easily discernible. It is also interesting to note that the percentage of spoilt work was particularly high at this period. This spurt seems more marked in the case of the semi-automatic workers, than in the case of the handworkers (of Figures 1 and 2). It should also be noted that the level of output for the semi-automatic after the spurt following the change tends to revert to its original level, whereas the level of output for the hand-workers, although it drops from its initial spurt, tends to assume a higher level than that previously maintained. Possibly the increase in output with handworkers is less affected by the transitory effects of the spurt, and more dependent upon the actual lessening of the fatigue of the worker. Handwork depends more upon human effort than does semi-automatic work and therefore reflects more clearly the conditions affecting fatigue. It may be presumed that both hand and semi-automatic workers have a desire to obtain equal results from the shorter shift as from the longer; in the case of the handworker his lessened fatigue will allow of his putting this desire into operation, wheras in the case of the machine worker, owing to the smaller part played by human effort, the increase in output,

apart from the initial spurt, is less. When the standard of increased output is maintained over a long period in a process like glassblowing, we may assume that it is connected with some fundamental law affecting bodily rhythm. When, however, it tends to pass away after a short period, we may assume that it is due mainly to voluntary effort, and by the nature of things, spurts due to volition must ultimately drop to the level of the normal bodily activity.

Seasonal Variation.

There is a general opinion in the glass trade that output is unfavourably affected by hot weather. Figure 2 gives the mean temperature for each month for the years 1918-1920 together with the output records of a special article manufactured by the factory in question almost continuously throughout the period. It will be noted that there is a tendency for output to fall when the temperature and, vice versa, the correlation between the two lines is $+.35 \pm .117$. Similar records were obtained from other factories, but the lines of output were in no cases so continuous as the one shown in Figure 2, although the tendency was in all cases the same, and so in order not to complicate the figure unnecessarily they have not been included. It is clear that temperature does affect output, and this can also be seen in Figure 3, which shows the effect of the breakdown of the apparatus for blowing cold air into the mouth of the gathering hole which occurred during the progress of an investigation at our factory. The difference between the two lines shows the longer time taken to manufacture each gross of bottles when the worker was exposed to the direct heat from the tank. The lines tend to diverge more as the day continues, from which we may conclude that the cumulative effect of adverse temperature conditions causes a more rapid onset of fatigue. The most satisfactory way of further investigating the connection between fatigue and temperature with a view to determining the most efficient method of ventilation for glass works is by means of the kata-thermometer. Most glass factories are provided with systems of artificial ventilation, but in some cases the workers have an objection to using them. In a record such as is given

in Figure 2 there is no means of saying whether the apparatus for artificial ventilation was or was not employed at any particular time. In an intensive investigation with the kata-thermometer this would be known, and it is possible that an even closer connection may be discovered between fatigue and the cooling power of the air in which glass blowers work.

The connection between temperature and output found by Vernon in the iron and steel and tinplate industries coincides with that found in the glass trade. (See Industrial Fatigue Research Board Reports, Nos. 1 and 5.)

Comparative Efficiency of Shifts.

Figure 4 shows the relative efficiency of the three shifts throughout the year at one factory. Figures 5, 6, 7 show the relative efficiency of the three shifts at three factories throughout the week. These four figures all agree in showing that the morning shift is the least efficient. The morning shift in all cases except one begins at 6 a.m. and ends at 2 p.m. In one factory it began at 7 a.m. and ended at 3 p.m. The possible cause of this relative inefficiency may be that the workers go to the factory without a proper breakfast. Considerable disorganisation would be caused in the household if breakfast was properly prepared and eaten in sufficient time for the worker to be in the factory by 6 a.m., and perhaps on this account the meal tends to be scanty and hurriedly eaten. Another reason for the comparative inefficiency of the morning shift may be that the hottest period of the day occurs towards the end of this shift when, as is shown in Figure 3, the workers are more liable to feel the adverse effects of high temperature owing to increasing fatigue. There is a marked fall off in the output of the morning shift shown in Figure 4 during the summer months, which also goes to show that temperature affects the output of this shift more than the others.

The night shift is, on the whole, less efficient than the afternoon shift, although there are exceptions to this. The difference is, however, not very great and should be compared with the difference between day and night work shown in Figure 8,

which represents the daily output of a factory working the alternative shift system of six hours on and six hours off during the 96 hours of the working week (Monday to Thursday). It will be seen that the night shift is always less efficient than the day shift, that its efficiency declines more towards the end of the week than does that of the day shift, and that there is always more lost time on the night shifts than the day shifts. It must obviously be very fatiguing to work 12 hours out of the 24, even if it is divided into two six-hour shifts, and this fatigue seems to show itself in accentuating the difference between day and night work to the great disadvantage of the latter. This difference in efficiency is also shown in Figure 9. On only one occasion during the summer is the night shift better than the day. Throughout the year the day shift is 6.1 per cent. better than the night shift.

Daily Variation in Output.

The daily variations were obtained from the firms visited, but they revealed no very striking features, in the case of either the two or three-shift system. Figure 10 shows the percentage variation for the ten-hour shift and the eight-hour shift, and the alternative six-hour shift for four working days of the week. The method adopted is to find the mean of the daily output and express any variation from this mean as a percentage. By this method curves of output become directly comparable with each other and differences which they manifest are possible indications of workers' fatigue. It will be seen in Figure 10 that the curves representing both the ten and eight-hour shifts (the average of output of the two most reliable sets of records) show comparatively small deviation from their means, the eight-hour shift showing least. The curve representing the alternative six hour-shift method shows considerable variation in Monday's and Thursday's level. If this method of measuring fatigue is valid we may infer that the alternative method of working is far more fatiguing than either of the other two.*

*British Psychological Journal (General Section), Vol. XIII., Part 3, January 7th, 1923. "Interpretation and Plotting of Output Curves,' by Eric Farmer, page 308.

Hourly Variation.

Various records of hourly variation were taken, but as it was impossible to use these for the purpose of the comparative efficiency of the shifts, and since they showed no features of special interest they have not been incorporated in the report. Their general tendency was a "warming-up" period at the beginning of the shift with a tendency to fall away towards the end, and in most cases there was a short end spurt.

Figure 11 is given in order to show the effect of rest pauses during the working day. It was obtained by timing the output of a steady worker ten times every quarter of an hour during the afternoon shift for three consecutive days. It will be noticed that the tea pause of half an hour checks the rise of the curve representing the time required to manufacture the bottle in question, and for some time after that a stable condition of work is maintained. The ten-minute break towards the end of the shift has the effect of considerably reducing the time required to manufacture the article.

The American System.

Records were obtained from one firm during the investigation concerning the effect of the change of working hours on the American System. In this system the skilled men are employed purely on skilled operations, all other work connected with the manufacture of the bottle being done by unskilled workers. This method of working produces a much higher output, in some cases amounting almost to 100 per cent. The effect of the change of working hours on this system is given in Table V. and Va., and it will be seen that there is a considerable increase in output, which is also accompanied by a slight increase in the amount of spoilt work. This increase is partly due to the initial spurt following the change shown in Figure 12, but it is also to be noted that when stability is attained after the spurt the curve of output is on a higher level than it was before the change. Part of the increase in spoilt work is undoubtedly due to the spurt since during that period the amount of spoilt work was higher than either before or after.

*The percentage increase in output on these small bottles is about on the same level as that obtained in other works on bigger bottles, and if the inference drawn from previous data that the increased output due to the shortening of hours is more marked in heavier than in lighter work, we may infer that the increase for heavier bottles under the American system would be proportionately larger.

Summary.

1. Within the limits of the data obtained during this inquiry it is clear that the relative hourly efficiency in bottle blowing has been increased by shortening the hours of work, though this increase is in no case so great as to bring the output of the eight-hour shift to the level of the ten-hour shift. It must, however, be borne in mind that the plant in factories employing the three-shift system is being productively used for 24 hours per day, whereas in factories employing the two-shift system it is only being productively used for 20 hours a day. From this it follows that the total output per day is greater with the three-shift system than with the two-shift system.

2. Night work in the three-shift system does not appear to put a markedly greater strain on the men than day work. The night shift is always more efficient than the morning shift, and not much less efficient than the afternoon shift. When 12 hours work out of 24 hours is done in alternate six-hour shifts, night work is consistently less efficient than day work.

3. There is evidence of seasonal variation in output and there can be little doubt that a more detailed inquiry into the effect of temperature on output could be undertaken. In order to do this satisfactorily it would be necessary to take katathermometer readings in various factories at various times of the day and at various seasons of the year. The practical outcome of such an inquiry would be to throw some light on the most efficient method of artificial ventilation.

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*No records for heavier bottles were obtainable.

4. An interesting experiment with a view to relieving fatigue and increasing efficiency could be carried out by alternating the work of each member of a "chair." At present the same work is done throughout the whole shift by each member of the group. The task of gathering the molten glass from the pot is undoubtedly the most exhausting process and yet the rate of production is almost entirely dependent on the worker who performs this operation. It is probable that fatigue could be considerably relieved if the men took turns at this. In some of the subsidiary processes the worker sits down so that an alternation in the method of working would involve a change from a standing to a sitting position which would probably have beneficial results.

5. The very greatest care has been exercised in this inquiry only to utilise reliable data. Much of the data obtained was not made use of because it contained interfering factors, the effect of which could not be determined. For this reason the data are not so voluminous as might be desired, but they are undoubtedly of a kind from which conclusions can be safely drawn.

Appendix I.

The Effect of Practice.

Figure 13 is given in order to show the part played by practice effects in the manufacture of glass bottles. The data were obtained from a factory employing a semi-automatic process of bottle manufacture, and give the average output per shift each week until relative stability is attained. The earlier weeks are not included, as during this period the workers in question were suffering from difficulty with their moulds. The bottle being made was one of which the firm manufactured a considerable quantity, but there had been a stoppage in its manufacture for some time previous to this period. A and C were both experienced gatherers and had previously been employed on the manufacture of this particular bottle. B had never previously been employed as a gatherer. It will be noted that it is not until the tenth week that equilibrium is reached and it is also interesting to note that B, although he had had no previous experience in gathering is very little behind the others in efficiency, and when stability is finally reached is practically equal to them. This figure is given in order to show how much more economic it is to manufacture long runs of the same article, and with what comparative ease a beginner can acquire sufficient skill to become an efficient gatherer. The skill employed in gathering appears to lie more in judging the amount of glass necessary for the particular article than in its actual manipulation. All three gatherers take approximately ten weeks to become accustomed to this, and previous experience seems to play very little part in it. This figure should be compared with Figure 14.

Appendix II.

The Effect of Stoppages.

Figure 14 shows the effect on output of two stoppages in a glass works during 1921. The first was due to the coal strike and the second to the influenza epidemic. The average efficiency of both shifts is lower after the long stoppage due to the coal strike and the efficiency of the day shift is lower after the stoppage due to influenza, though that of the night shift is higher. The loss of efficiency through stopping is probably caused by the men losing to some extent their motor dexterity through want of practice.

The data contained in Figure 13 are sufficient to show that this is the case, and the evidence obtained from this other factory corroborates it. It should, however, be borne in mind that part of the drop after the coal strike may have been due to the hot weather.

TABLE I.

SHOWING THE EFFECT OF SHORTENED HOURS ON HOURLY OUTPUT.

Factory.	Bottle.	10 Hour Shift.				8 Hour Shift.				Percentage.		Period over which Records were taken.	
		Output per Shift.	No. of Records.	Standard Deviation.	Hourly Output.	Output per Shift.	No. of Records.	Standard Deviation.	Hourly Output.	Increase.	Decrease.	10 hour Shift.	8 hour Shift.
1.	1 oz. Vial ...	1907	10	64.7	200.7	1428	29	61.8	196.9	—	1.9	Jan., 1917-June, 1917	Jan.-Mar. and Oct.-Dec. 1921
	6 oz. Flats ...	1466	90	99.6	153.6	1109	74	75.8	152.9	—	0.5	Jan., 1917-Dec., 1918	July, 1919-Dec., 1921
	8 oz. Flats ...	1389	85	99.6	145.4	1096	115	74.1	151.2	3.9	—	Jan., 1917-Dec., 1918	July, 1919-Dec., 1921
	20 oz. Corbyns	1081	7	82.4	113.8	902	10	57.7	124.4	9.3	—	1917 & 1918	1920 & 1921
	24 oz. Corbyns	1009	14	58.6	106.2	878	33	53.4	121.1	14.0	—	,,	,,
	32 oz. Corbyns	844	11	42.1	88.8	765	6	54.8	106.2	19.6	—	,,	,,
	80 oz. Corbyns	425.6	3	15.3	44.8	390.8	13	32.7	53.9	20.3	—	1918	,,
	90 oz. Corbyns	366.7	7	17.3	38.6	342.2	14	55.6	47.2	22.3	—	,,	,,
2.	2 oz.	2036.0	41	19.5	214.3	1736.1	25	60.5	239.4	11.7	—	Mar., 1918-Feb., 1919	Jan., 1920-Dec., 1920
	3 oz.	2002.6	40	59.6	210.8	1632.1	32	35.3	225.1	6.8	—	Mar., 1918-Feb., 1919	Jan., 1920-Dec., 1920
	4 oz.	1956.5	66	82.4	205.9	1567.8	144	34.2	216.2	5.0	—	Mar., 1918-Feb., 1919	Jan., 1920-Dec., 1920

Factory.	Bottle.	10 Hour Shift.				8 Hour Shift.				Percentage.		Period over which Records were taken.	
		Output per Shift.	No. of Records.	Standard Deviation.	Hourly Output.	Output per Shift.	No. of Records.	Standard Deviation.	Hourly Output.	Increase.	Decrease.	10 hour Shift.	8 hour Shift.
	6 oz.	1835.2	145	91.9	193.2	1486.3	243	39.2	205.1	6.2	—	Mar., 1918-Feb., 1919	Jan., 1920-Dec., 1920
	8 oz.	1818.8	382	85.2	191.4	1428.6	680	83.6	197.0	2.9	—	Mar., 1918-Feb., 1919	Jan., 1920-Dec., 1920
	10 oz.	1662.8	13	54.3	175.0	1354.0	38	68.1	186.7	6.6	—	Mar., 1918-Feb., 1919	Jan., 1920-Dec., 1920
	12 oz.	1564.3	30	34.4	164.6	1276.2	56	51.9	176.0	6.9	—	Mar., 1918-Feb., 1919	Jan., 1920-Dec., 1920
	16 oz.	1326.4	8	7.1	139.6	1143.9	19	39.4	155.8	11.6	—	Mar., 1918-Feb., 1919	Jan., 1920-Dec., 1920
3.*	4 oz. Flats ...	133.6	203	8.7	14.0	111.0	414	7.3	15.9	8.9	—	Mar., 1918-Feb., 1919	April, 1920-Mar., 1921
	10 oz. Rounds	112.6	52	6.4	11.8	95.2	64	5.9	13.1	10.9	—	Mar., 1918-Feb., 1919	April, 1920-Mar., 1921
	Pints	100.6	76	14.2	10.6	89.9	112	6.5	12.2	15.7	—	Sept., 1918-June, 1919	Sept., 1919-June, 1920
	10 oz. Codds.	89.2	108	8.7	9.4	77.2	34	4.3	10.6	12.9	—	Mar., 1918-Feb., 1919	April, 1920-Mar., 1921
4.	6 oz. Medical	1427.8	18	93.8	150.6	1219.5	42	77.9	169.7	12.6	—	1917	1920
	8 oz. Medical	1330.5	43	93.4	140.4	1143.0	86	65.6	159.5	13.6	—	,,	,,

* Output in this factory is given in dozens.

TABLE II.

SHOWING THE EFFECT OF SHORTENED HOURS ON PERCENTAGE OF WORK SPOILT.

		10 Hour Shift.						8 Hour Shift.						Difference.	
Factory.	Bottle.	Declared.	Standard Deviation.	Drawn.	Standard Deviation.	No. of Records.	Per cent. Spoilt.	Declared.	Standard Deviation.	Drawn.	Standard Deviation.	No. of Records.	Per cent. Spoilt.	Increase.	Decrease.
2.	2 oz.	2036.0	19.5	1985.0	49.1	41	2.5	1736.1	60.5	1703.0	91.4	25	1.9	—	0.6
	3 oz.	2002.6	59.6	1928.6	83.2	40	3.7	1632.1	35.3	1582.3	120.4	32	3.1	—	0.6
	4 oz.	1956.5	82.4	1885.1	89.7	66	3.6	1567.8	34.2	1519.4	107.0	144	3.1	—	0.5
	6 oz.	1835.2	91.9	1784.1	33.2	145	2.8	1486.3	39.2	1438.8	122.8	243	3.2	0.4	—
	8 oz.	1818.8	85.2	1762.1	98.1	382	3.1	1428.6	83.6	1380.6	87.3	680	3.4	0.3	—
	10 oz.	1662.8	54.3	1632.5	66.1	13	1.8	1354.0	68.1	1305.0	70.1	38	3.6	1.8	—
	12 oz.	1564.3	34.4	1529.3	51.1	30	2.2	1276.2	51.9	1220.9	60.4	56	4.3	2.1	—
	16 oz.	1326.4	7.1	1312.5	10.0	8	1.0	1143.9	39.4	1098.9	41.2	19	3.9	2.9	—
3.	4 oz. Flats ...	132.5	12.5	125.9	12.5	209	5.2	109.8	6.2	105.1	6.3	321	4.5	—	0.7
4.	6 oz. Medicals	1427.8	93.8	1349.1	102.5	18	5.5	1219.5	77.9	1147.6	74.0	56	5.9	0.4	—
	8 oz. Medicals	1330.5	93.4	1227.9	109.0	43	7.7	1143.0	65.6	1101.4	95.7	86	8.9	1.2	—

TABLE III.
SHOWING THE EFFECT OF SHORTENED HOURS ON TIME LOST THROUGH ABSENCE.

Factory.	Absences of.	10 Hour Shift.			8 Hour Shift.			
		Percentage Time Lost Monthly.	Standard Deviation.	No. of Records.	Percentage Time Lost Monthly.	Standard Deviation.	No. of Records.	Decrease.
1.	Under 4 consecutive weeks ...	3.15	1.76	24	3.05	1.43	22	0.10
	2 days and under	1.31	0.47	24	1.15	0.59	22	0.16

TABLE IV.
SHOWING THE EFFECT OF SHORTENED HOURS ON HOURLY OUTPUT FOR SEMI-AUTOMATIC MACHINES.

Factory.	Bottle.	10 Hour Shift.				8 Hour Shift.				Percentage.		Period over which records were taken.	
		Output per Shift.	No. of Records.	Standard Deviation.	Hourly Output.	Output per Shift.	No. of Records.	Standard Deviation.	Hourly Output.	Increase.	Decrease.	10 Hour Shift.	8 Hour Shift.
3.	2 lb. Jam (Duens) ...	148.9	332	15.0	15.65	119.4	363	9.3	16.48	5.3	—	Oct., 1918-July, 1919	Aug., 1919-Mar., 1920
5.	2 lb. Jam (Duens) ...	100.1	93	13.7	10.54	103.2	381	7.3	14.26	35.3	—	Sept., 1916-April, 1917 & Feb., 1919 July, 1919	Aug., 1919-Aug., 1920
6.	Pints	96.2	481	7.0	10.13	77.6	231	4.6	10.70	5.6	—	Dec., 1919-Dec., 1921	Dec., 1921-Nov., 1922
	Quarts	80.0	1014	8.6	8.42	67.3	376	5.7	9.28	10.2	—	Jan., 1920-Nov., 1921	Dec., 1921-Nov., 1922

TABLE IVa.

SHOWING THE EFFECT OF SHORTENED HOURS ON PERCENTAGE OF WORK SPOILT FOR SEMI-AUTOMATIC MACHINES.

		10 Hour Shift.						8 Hour Shift.						Difference.	
Factory.	Bottle.	Declared.	Standard Deviation.	Drawn.	Standard Deviation.	No. of Records.	Per cent. Spoilt.	Declared.	Standard Deviation.	Drawn.	Standard Deviation.	No. of Records.	Per cent. Spoilt.	Increase.	Decrease.
3.	2 lb. Jams ...	148.9	15.0	135.8	16.9	332	10.6	119.4	9.3	109.4	12.7	363	8.8	—	1.8
5.	2 lb. Jams ...	100.1	13.7	95.3	16.1	92	7.4	103.2	7.3	96.9	8.2	381	7.3	—	0.1
6.	Pints	96.2	7.0	89.4	6.8	481	7.8	77.6	4.6	68.9	5.5	231	15.8	8.0	—
	Quarts	80.0	8.6	72.21	9.3	1014	13.5	67.3	5.7	59.8	6.2	376	16.1	2.6	—

TABLE V.

SHOWING THE EFFECT OF SHORTENED HOURS ON THE HOURLY OUTPUT FOR AMERICAN SYSTEM.

Factory.	Bottle.	10 Hour Shift.				8 Hour Shift.				Percentage.		Period over which Records were taken.	
		Output per Shift.	No. of Records.	Standard Deviation.	Hourly Output.	Output per Shift.	No. of Records.	Standard Deviation.	Hourly Output.	Increase.	Decrease.	10 Hour Shift.	8 Hour Shift.
3.	5 oz.	230.3	239	16.6	24.27	188.6	568	18.7	26.34	8.5%	—	Oct., 1918-July, 1919	Sept., 1919-Nov., 1920
	8 oz.	206.5	162	21.3	22.03	174.3	458	15.3	24.70	12.1%	—	Feb., 1919-July, 1919	Sept., 1919-Dec., 1920

TABLE VA.

SHOWING THE EFFECT OF SHORTENED HOURS ON PERCENTAGE OF WORK SPOILT FOR AMERICAN SYSTEM.

Factory.	Bottle.	10 Hour Shift.						8 Hour Shift.						Difference.	
		Declared.	Standard Deviation.	Drawn.	Standard Deviation.	No. of Records.	Per cent. Spoilt.	Declared.	Standard Deviation.	Drawn.	Standard Deviation.	No. of Records.	Per cent. Spoilt.	Increase.	Decrease.
3.	5. oz.	230.3	16.6	217.2	17.7	239	5.7	188.6	18.7	175.5	22.1	568	7.1	1.4	—
	8 oz.	206.5	21.3	191.9	21.9	162	6.5	174.3	15.3	157.3	19.6	458	10.3	3.8	—

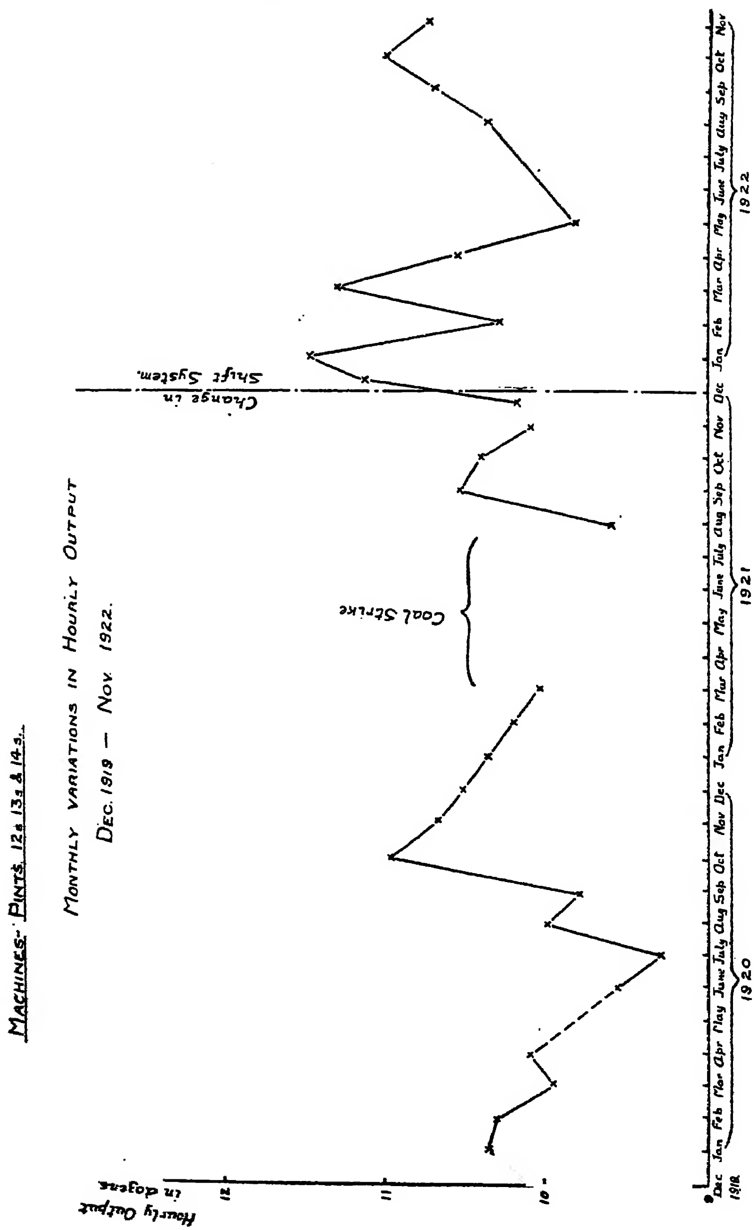

MACHINES: PINTS. 12s 13s & 14s.
MONTHLY VARIATIONS IN HOURLY OUTPUT
DEC. 1919 — NOV. 1922.
Coal Strike
Change in Shift System.
Hourly Output in dozens
10
11
12
Dec 1918
Jan Feb Mar Apr May June July Aug Sep Oct Nov Dec
1920
Jan Feb Mar Apr May June July Aug Sep Oct Nov Dec
1921
Jan Feb Mar Apr May June July Aug Sep Oct Nov
1922

FIGURE 1.

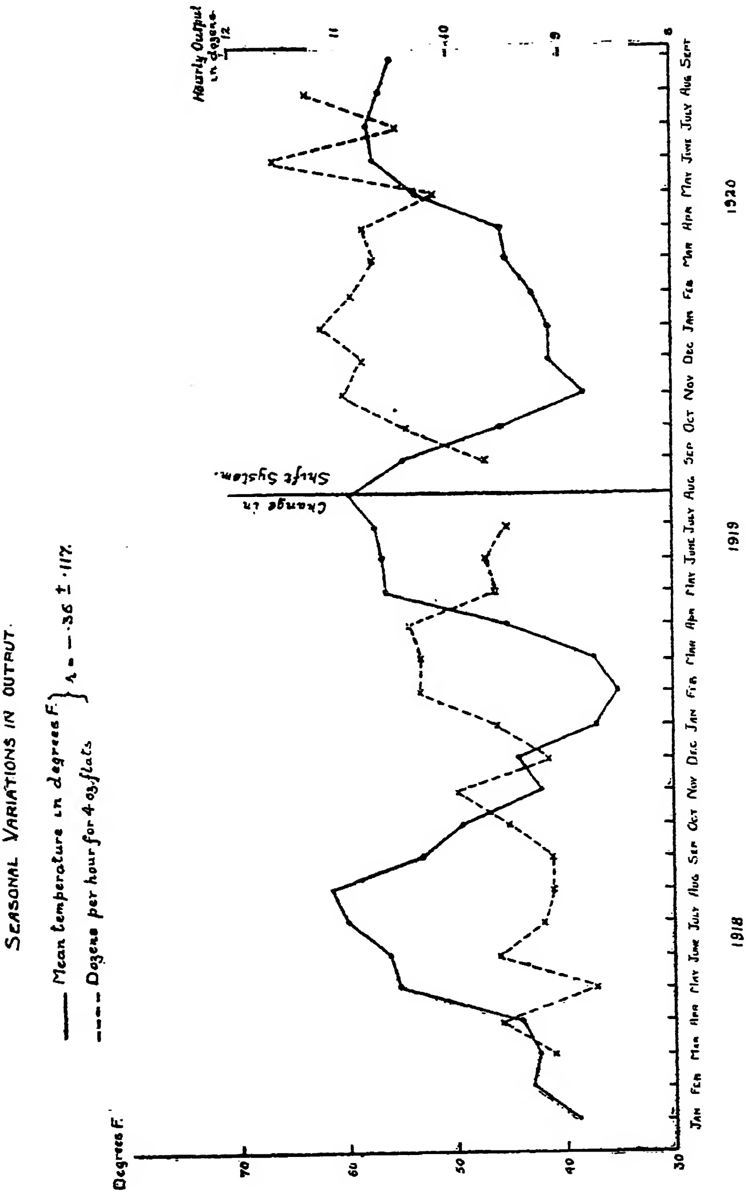

SEASONAL VARIATIONS IN OUTPUT.
Mean temperature in degrees F.
Dozens per hour for 4 oz. flats
r = −·36 ± ·117.
Degrees F.
30
40
50
60
70
Hourly Output in dozens
8
9
10
11
12
Change in Shift System.
JAN FEB MAR APR MAY JUNE JULY AUG SEP OCT NOV DEC
1918
1919
1920

FIGURE 2.

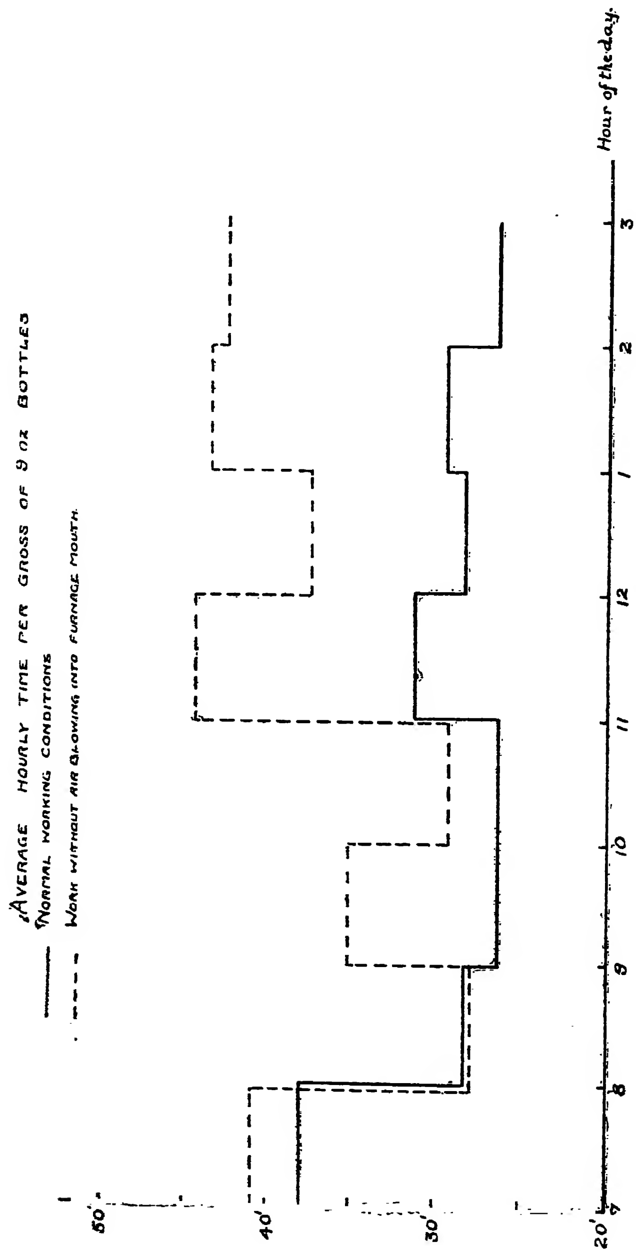

AVERAGE HOURLY TIME PER GROSS OF 9 OZ BOTTLES
NORMAL WORKING CONDITIONS
WORK WITHOUT AIR BLOWING INTO FURNACE MOUTH
Hour of the day
50'
40'
30'
20'
7
8
9
10
11
12
1
2
3

FIGURE 3.

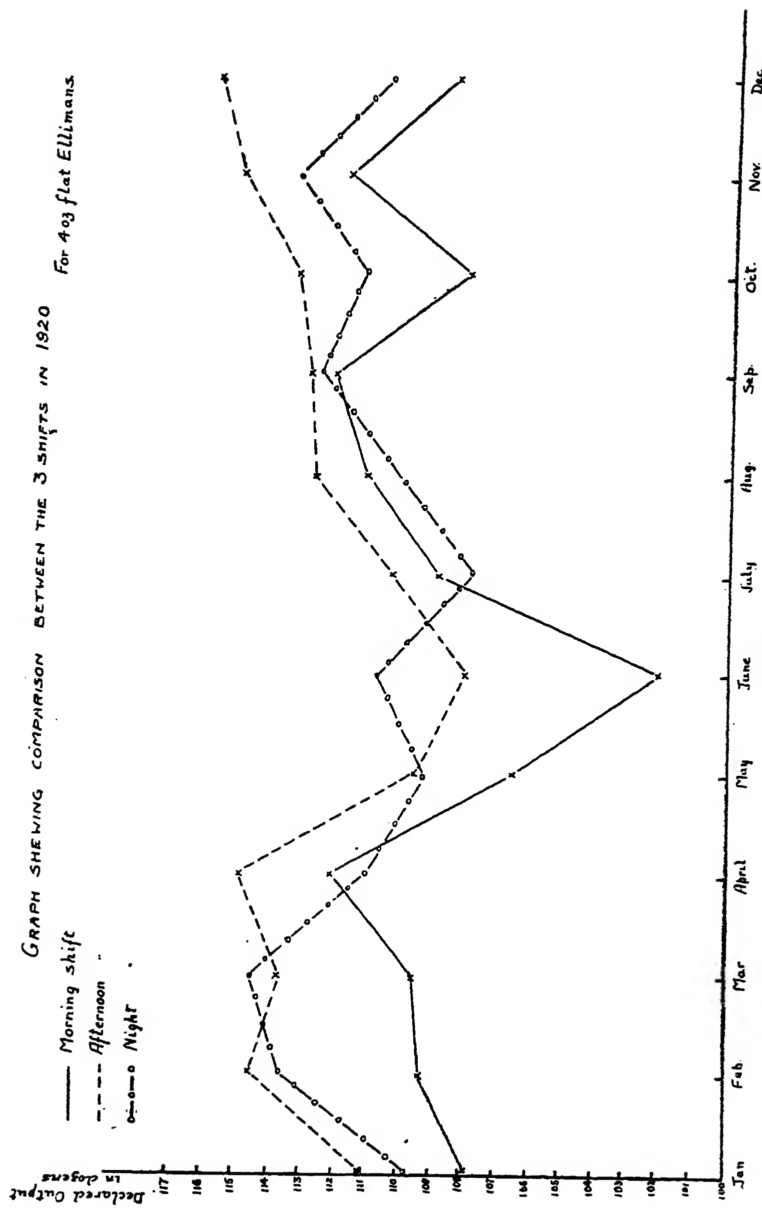

Graph shewing comparison between the 3 shifts in 1920
For 403 flat Ellimans
Morning shift
Afternoon "
Night "
Declared Output in dozens
117
116
115
114
113
112
111
110
109
108
107
106
105
104
103
102
101
100
Jan
Feb
Mar
April
May
June
July
Aug.
Sep.
Oct.
Nov.
Dec.

FIGURE 4.

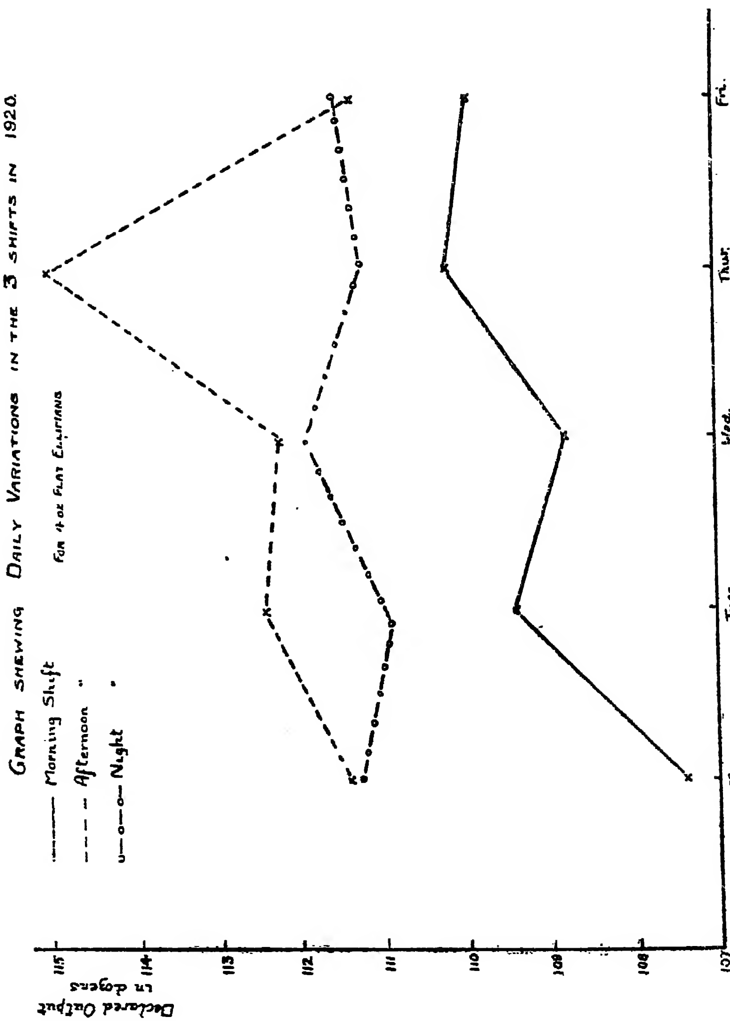

Graph shewing Daily Variations in the 3 shifts in 1920.
For 4 oz Flat
Morning Shift
Afternoon "
Night "
Declared Output in dozens
115
114
113
112
111
110
109
108
107
Mon
Tues
Wed.
Thur.
Fri.

FIGURE 5.

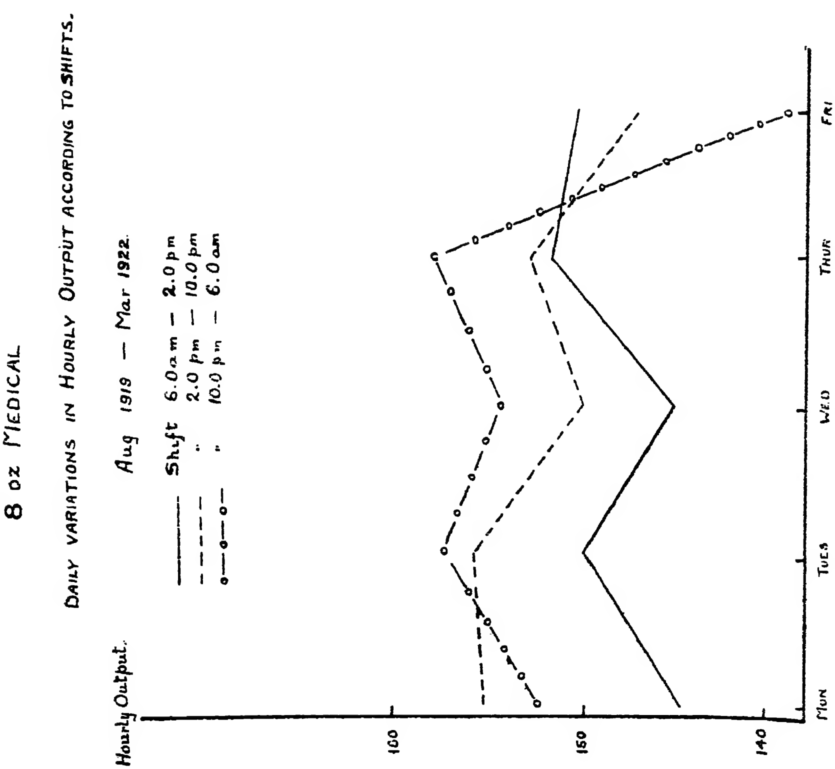

8 oz Medical
Daily variations in Hourly Output according to Shifts.
Aug 1919 — Mar 1922.
Shift 6.0 am — 2.0 pm
" 2.0 pm — 10.0 pm
" 10.0 pm — 6.0 am
Hourly Output.
160
150
140
Mon
Tues
Wed
Thur
Fri

Figure 6.

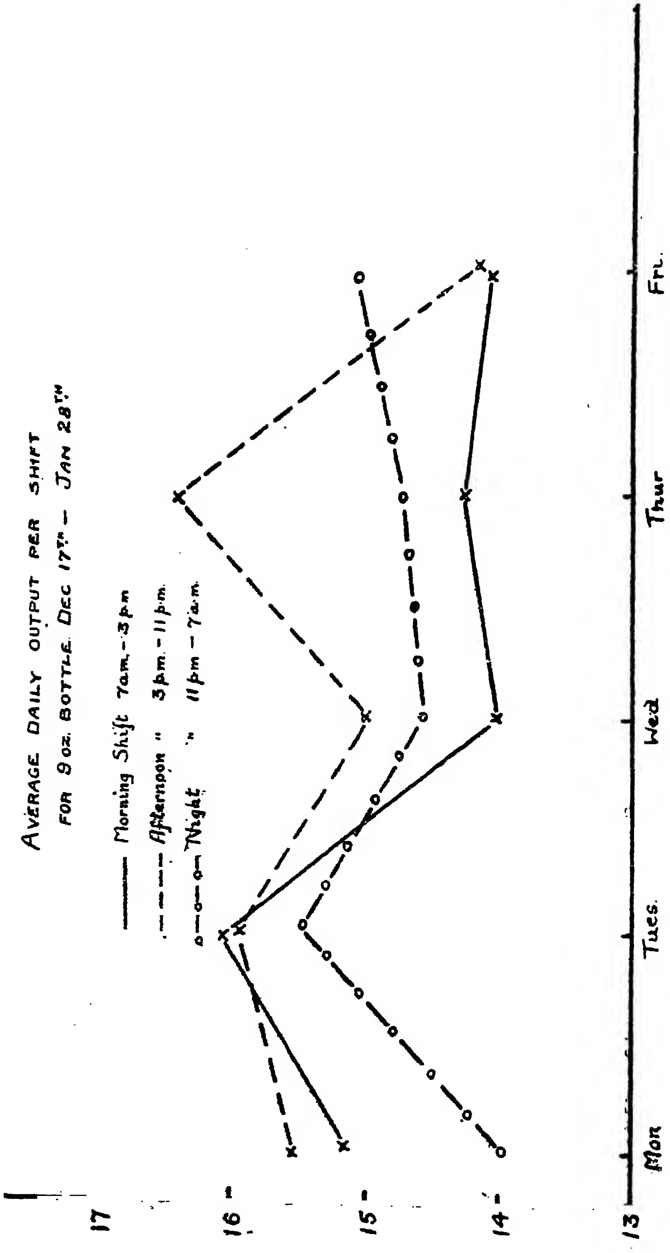
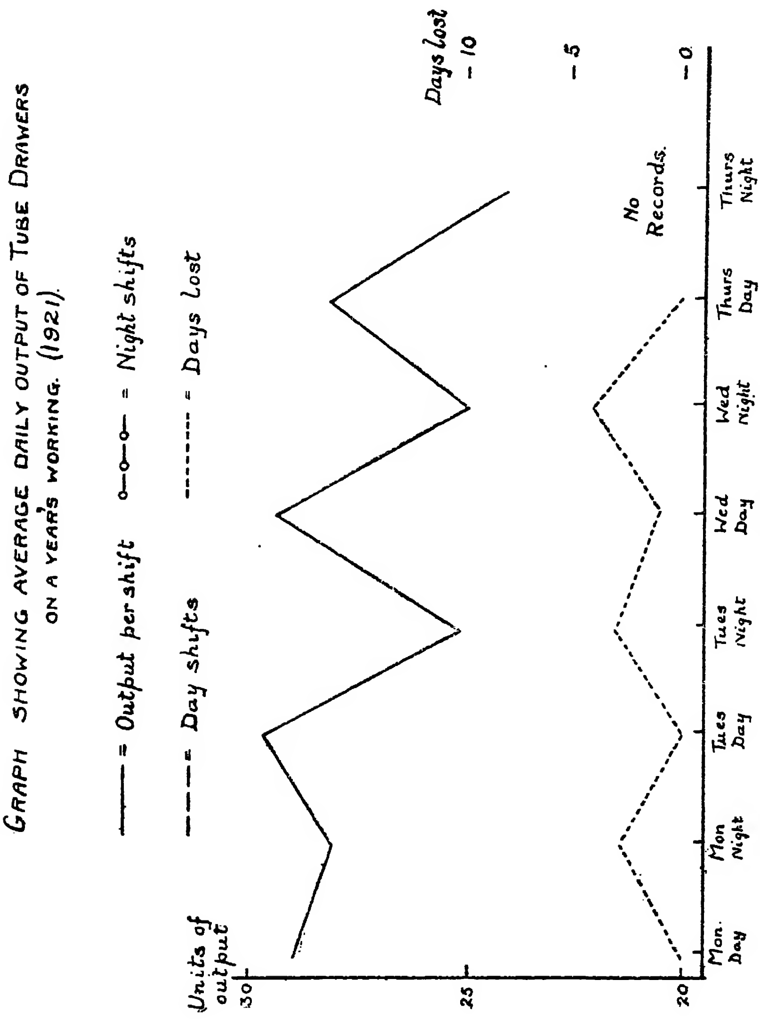

AVERAGE DAILY OUTPUT PER SHIFT
FOR 9 oz. BOTTLE DEC 17TH — JAN 28TH
Morning Shift 7a.m.-3p.m.
Afternoon " 3p.m.-11p.m.
Night " 11p.m.-7a.m.
17
16
15
14
13
Mon
Tues.
Wed
Thur
Fri.

FIGURE 7.



GRAPH SHOWING AVERAGE DAILY OUTPUT OF TUBE DRAWERS ON A YEAR'S WORKING. (1921).
—— = Output per shift
o—o—o = Night shifts
– – – – = Day shifts
- - - - - - - = Days lost
Units of output
30
25
20
Days lost
10
5
0
No Records.
Mon. Day
Mon Night
Tues Day
Tues Night
Wed Day
Wed Night
Thurs Day
Thurs Night

FIGURE 8.

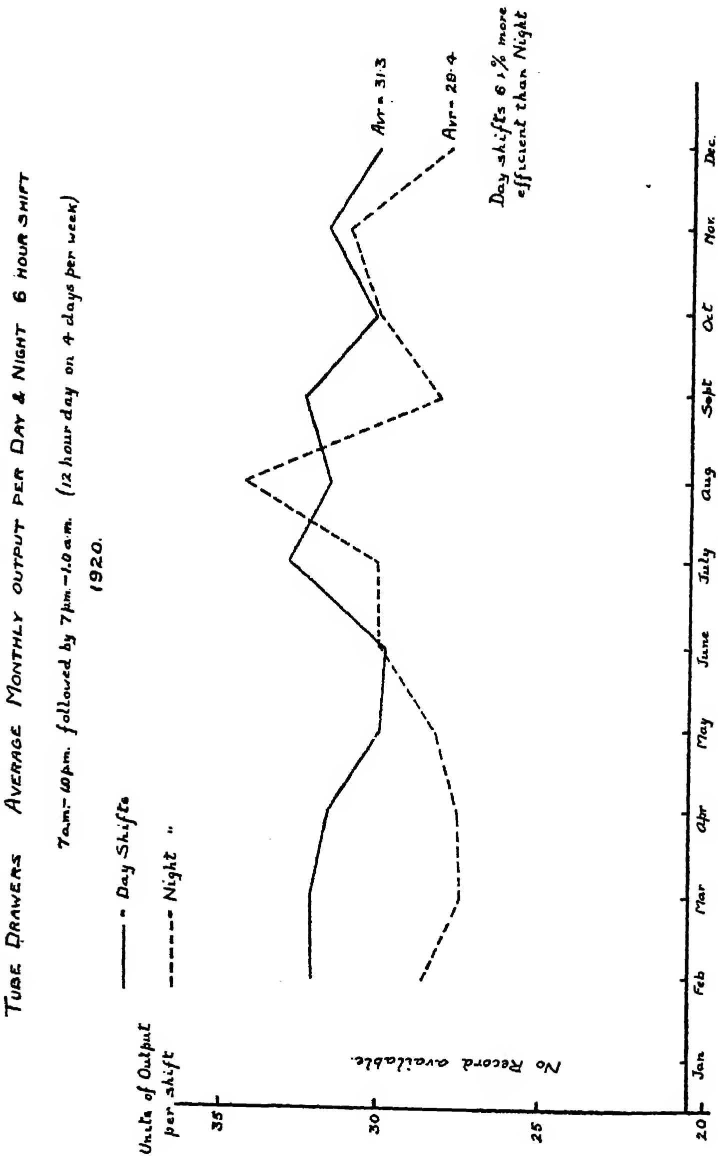

Tube Drawers Average Monthly output per Day & Night 6 hour shift
7 a.m.–1.0 p.m. followed by 7 p.m.–1.0 a.m. (12 hour day on 4 days per week)
1920.
Day Shifts
Night "
Avr = 31.3
Avr = 29.4
Day shifts 6.1% more efficient than Night
Units of Output per shift
No Record available.
35
30
25
20
Jan
Feb
Mar
Apr
May
June
July
Aug
Sept
Oct
Nov
Dec

FIGURE 9.

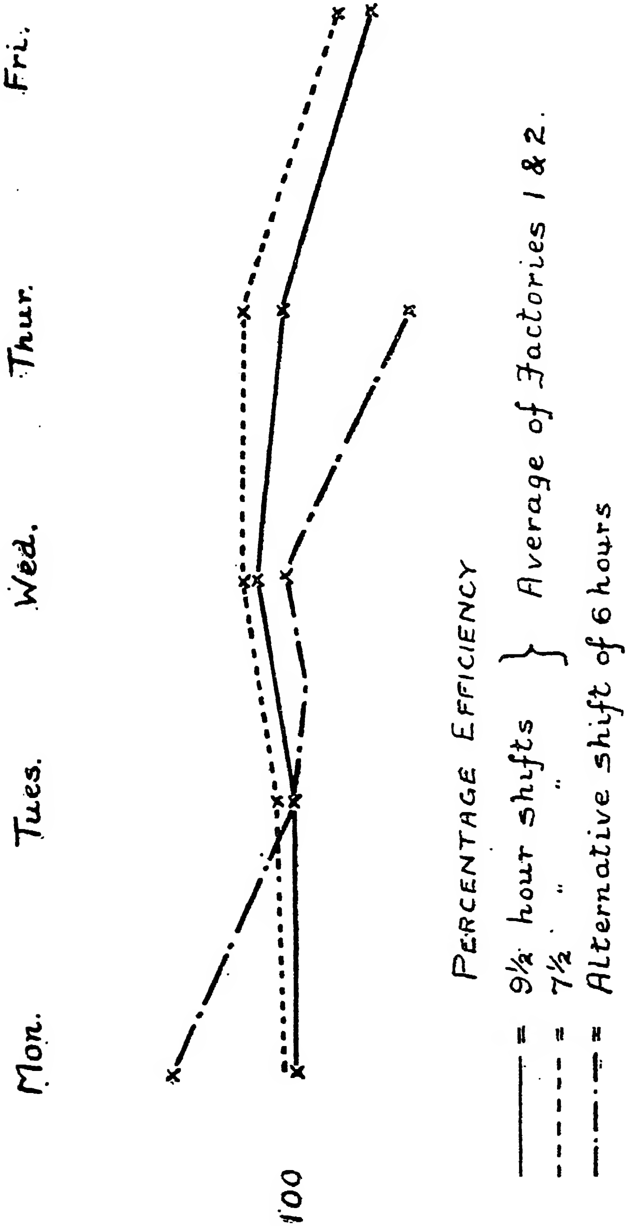

Mon.
Tues.
Wed.
Thur.
Fri.
100
PERCENTAGE EFFICIENCY
= 9½ hour shifts
= 7½ " "
Average of Factories 1 & 2.
= Alternative shift of 6 hours

FIGURE 10.

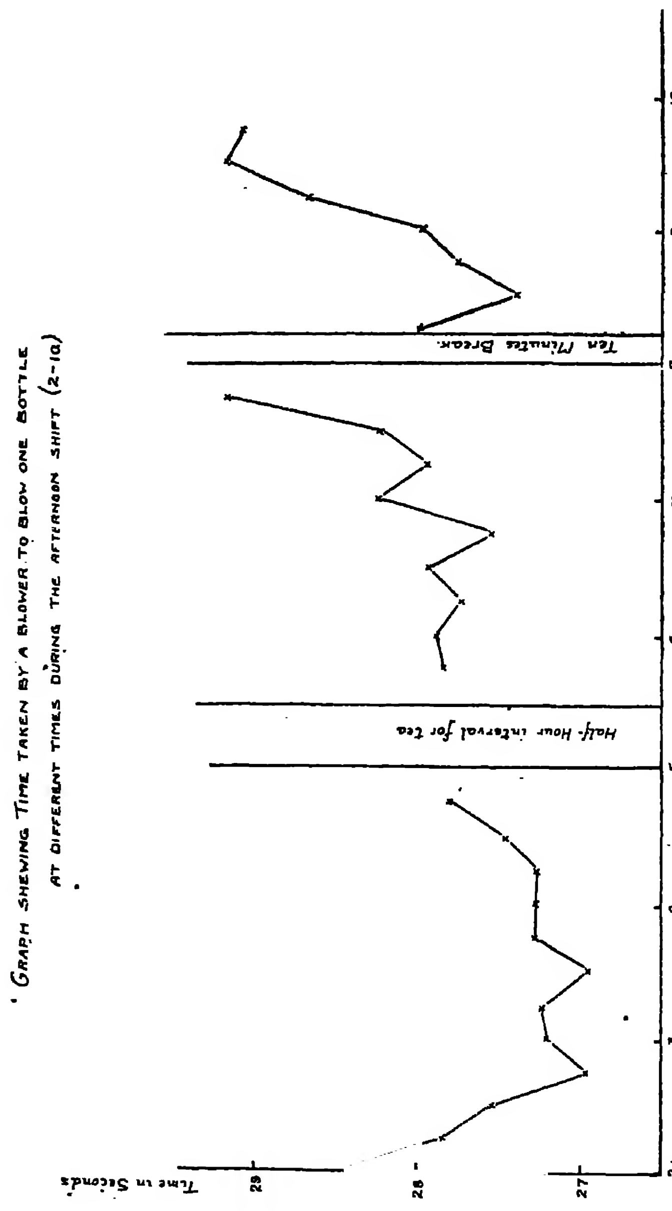

Graph shewing Time taken by a Blower to blow one Bottle at different times during the afternoon shift (2-10)
Time in Seconds
29
28
27
2 pm
3
4
5
6
7
8
9
10
Half-Hour interval for tea
Ten Minutes Break.

FIGURE 11.

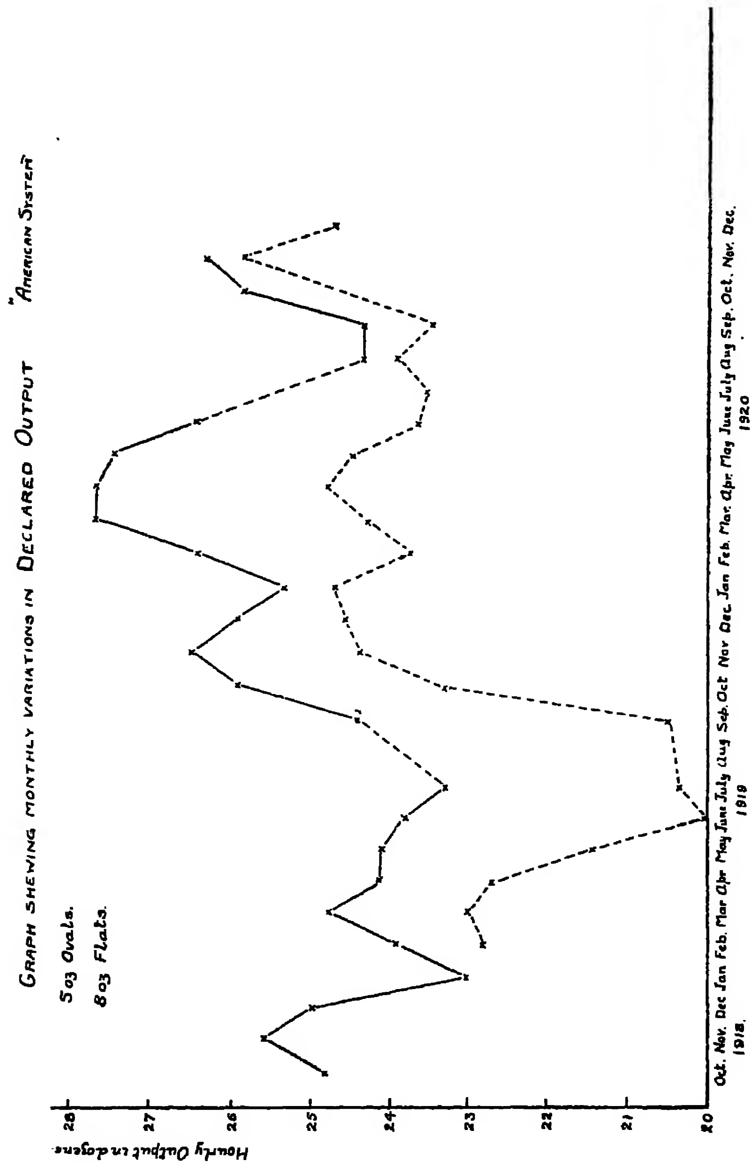

Graph shewing monthly variations in Declared Output "American System"
5oz Ovals.
8oz Flats.
Hourly Output in dozens
20 21 22 23 24 25 26 27 28
Oct. Nov. Dec Jan Feb. Mar Apr May June July Aug Sep. Oct Nov Dec Jan Feb. Mar. Apr. May June July Aug Sep. Oct. Nov. Dec.
1918
1919
1920

FIGURE 12.

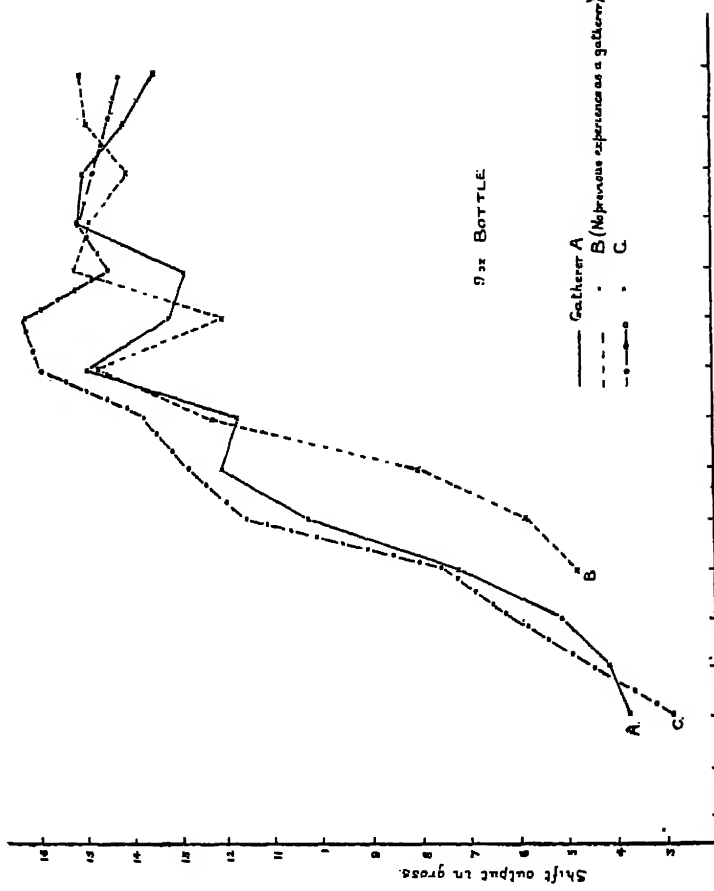
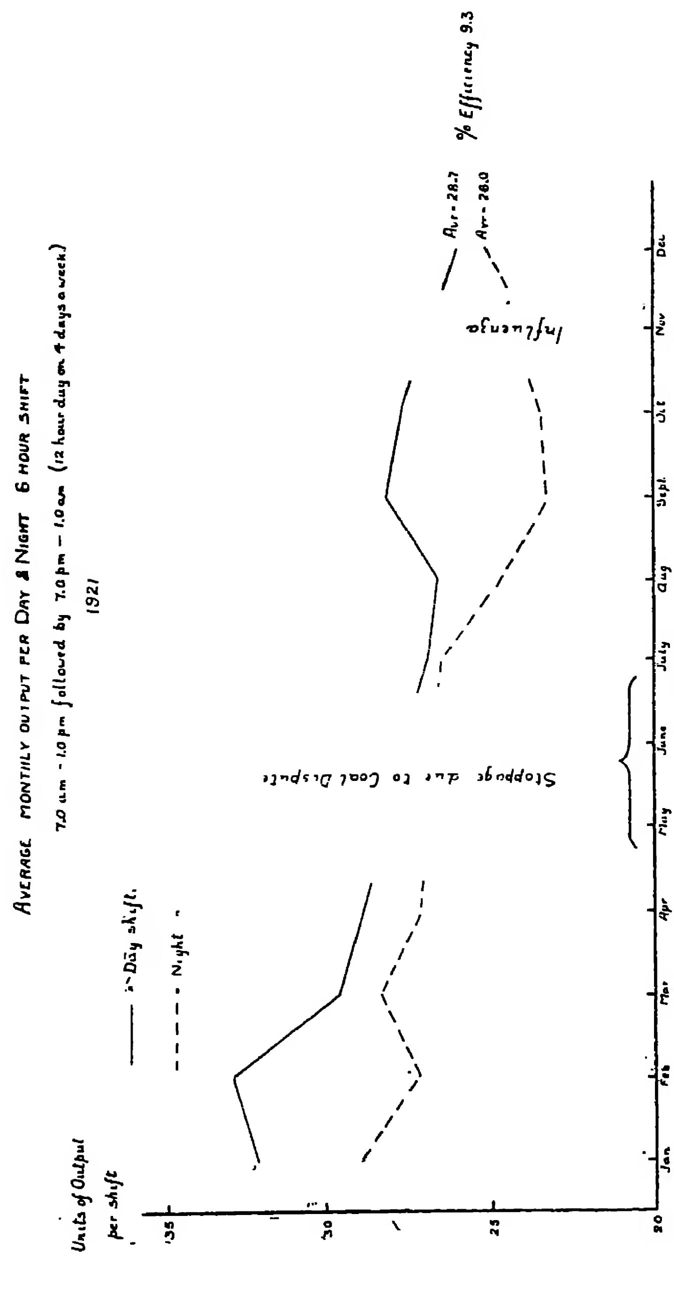

9 oz Bottle
Gatherer A
B (No previous experience as a gatherer)
C
Shift output in gross.

FIGURE 13.



Average Monthly Output per Day & Night 6 Hour Shift
7.0 a.m. - 1.0 pm followed by 7.0 pm - 1.0 am (12 hour day on 4 days a week.)
1921
Units of Output per shift
—— = Day shift.
- - - - " Night "
Stoppage due to Coal Dispute
Influenza
Av. - 28.7
Av. - 26.0
% Efficiency 9.3
35
30
25
20
Jan
Feb
Mar
Apr
May
June
July
Aug
Sept.
Oct
Nov
Dec

FIGURE 14.

GLASS RESEARCH ASSOCIATION BULLETIN.

No. 8. DECEMBER, 1923.

CONFIDENTIAL TO
THE MEMBERS OF
THE GLASS
RESEARCH
ASSOCIATION.

LONDON
GLASS RESEARCH ASSOCIATION,
50, Bedford Square, W.C. 1.

NOTE.

The Council of the Association does not hold itself responsible for the opinions expressed by the contributors of the various articles.

Contents.

I. Determinations of the Viscosity of Glass.

Programme of Research,
Ref.: Items 1, 2 *and* 7 (*a*).

PART III. (a).*

PREPARATION OF RODS.

Interim Report by the National Physical Laboratory on Investigations carried out on behalf of the Glass Research Association.

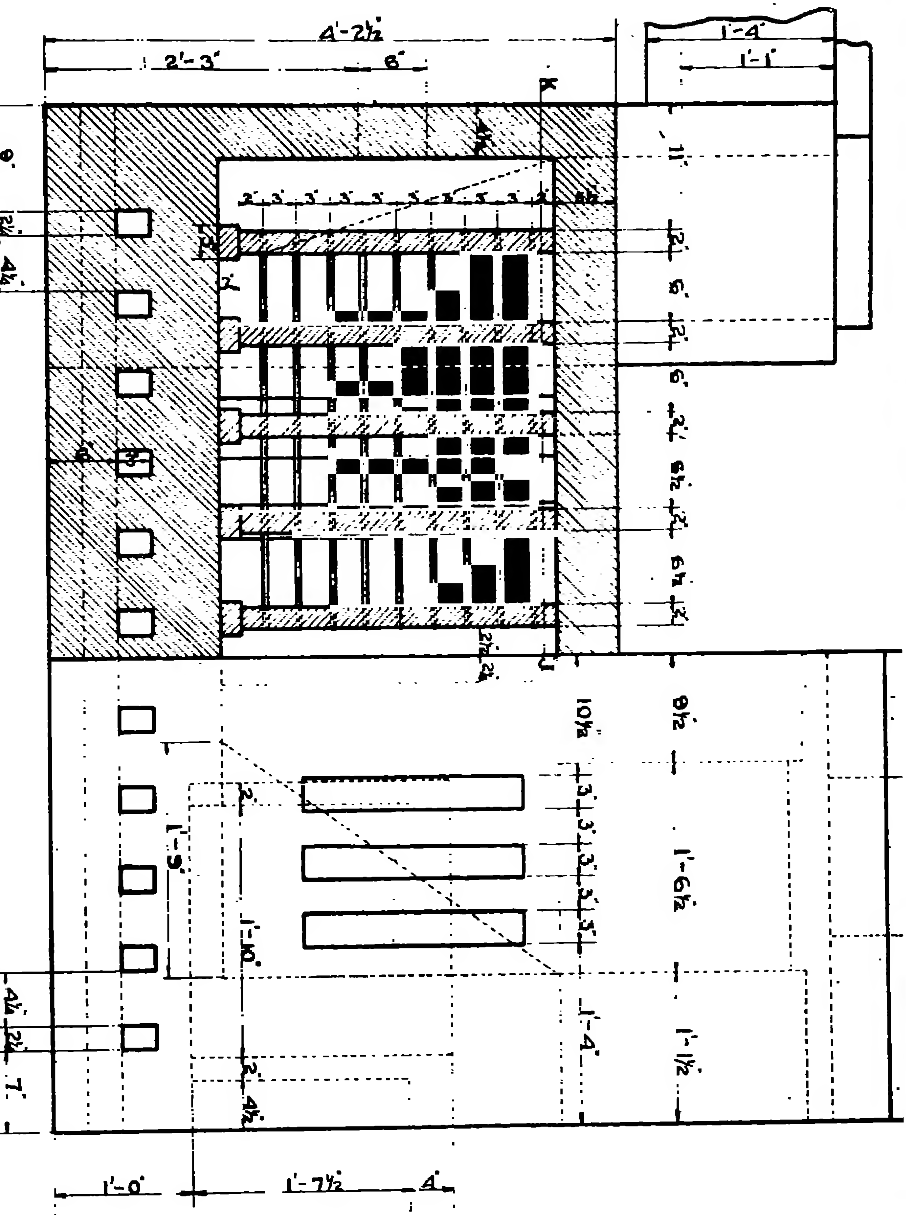
THE determination of the viscosity-temperature curves of glass at low temperatures requires as a preliminary the preparation of the glass in a convenient form, and a considerable amount of time has been spent on the problem of producing rods suitable for the measurement of low temperature viscosities. In the early stages of this work an attempt was made to prepare the rods by grinding on a lathe. Owing to the small diameter of the rods these efforts were not successful, and accordingly apparatus was constructed for drawing mechanically rods of various diameters which could be fused together to form the finished specimen. At the suggestion of the Director of Research, an apparatus was constructed on the lines of one which he had previously used for a similar purpose. The rod is drawn vertically from a pot of glass by drawing a bait through a long water-cooled tube. In this case the tube was made of aluminium, a metal extremely suitable for such a purpose. The internal diameter of the tube was 3-ins., except at the bottom, which was splayed out to meet an outer tube which had a diameter of 4¼-ins. Water circulated between the two tubes. The bottom of the tube was usually about 3-ins. from the surface of the glass. The bait, which hung from a Bowden cable, was raised slowly and uniformly by means of an electric motor. The rods were drawn with the heating supply shut off from the

* Determinations of the Viscosity of Glass, Part I, Glass Research Bulletin, No. 2.
Determinations of the Viscosity of Glass, Part II., Glass Research Bulletin, No. 5.

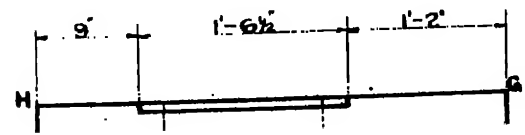
furnace, so that as the temperature dropped the diameter of the rod which was formed gradually increased.

A consideration of the conditions governing the formation of the rods shows that there is a fundamental obstacle to the production of accurately circular rods, and this difficulty becomes greater as the diameter of the rod increases. It results from hydrodynamical reasoning that the flow of glass in the pot leading to the formation of the rod tends to be greatest where the viscosity of the glass is highest. Since the water-cooled tube itself tends to produce a ring of glass the viscosity of which is lowest in the centre, there will be at all times a tendency for the rod to "run to the side." The danger of this event is increased by unsymmetrical temperature distribution or by heterogeneity of the glass. When the diameter of the rod is small its tendency to wander to the outside and to form unsymmetrical accretions is balanced by the effects of gravity and surface tension respectively. To minimise the difficulties it is advantageous to use wide shallow pots, those finally adopted having an internal diameter at the top of 10½-ins. and an internal height of 6½-ins. It is also necessary to prevent any rotation of the bait. The ease with which a good rod can be made in this way depends, amongst other things, on the extent of the "working range," and, whereas it is difficult to make a satisfactory rod of ½-in. diameter from a hard soda-lime glass, it is quite easy to make such a rod from a glass with a long working range such as St. 59.

The foregoing details have been given because the principles involved are common to other similar mechanisms, but it has been found necessary to abandon this method of rod making owing to the readiness with which the soda-lime glasses devitrify at the temperatures at which the process must be carried out. Before describing the process now used for the production of rods, a short reference may be made to the very successful furnace used for the preceding experiments. The furnace, as will be seen from Fig. 1, is of the recuperative type, and is of the same general design as that described by Rosenhain and Coad-Pryor in the Transactions of the Ceramic Society, Vol. XVIII. For ease in manipulating the glass the present furnace



4'-2½"
2'-3"
6"
1'-4"
1'-1"
11"
6"
6"
1'-6½"
1'-1½"
10½
9½
1'-4"
1'-10"
1'-9"
1'-0"
1'-7½"
4"



H
G
9"
1'-6½"
1'-2"

is provided with a large carborundum slab in the centre of the arch through which is a circular opening 15-ins. in diameter. If required, the glass can be melted inside a dense carborundum muffle having an internal diameter of 11½-ins., which enables lead glasses to be melted in open pots without danger of reduction. The furnace is very efficient and has the additional advantage of requiring no attention during the night. The distribution of temperature in the furnace is also very satisfactory.

To return to the question of rod-making, it has been pointed out that devitrification of the soda-lime glasses employed rendered necessary a change in procedure. Fortunately, at the time that this became apparent, the Optical Department of the Laboratory had extended their facilities for glass grinding, and it was found quite possible to prepare thoroughly satisfactory rods by direct grinding and polishing on a lathe. Rods are therefore now made by casting the glass into metal moulds and grinding to the required shape, a method which greatly reduces the danger of devitrification and which yields rods of truly circular section. In a future Report it is hoped to give results of measurements on rods produced in this way.

Work has been continued on the method of measuring viscosities described on page 11 of Bulletin No. 2. As was anticipated, the "Reactol" rod proved satisfactory, and it has been possible to measure viscosities as low as 10^5 C.G.S. units. China clay rods have also been used. Owing to the readiness with which glasses devitrify at the temperatures corresponding with these viscosities only a few measurements have been made in this way. The extension of the curve for glass St. 59 (See Fig. 10, Part III. (b).) to a temperature about 100° C. higher than that given in the previous Reports, results from the use of this method. The accuracy to be expected is of the same order as that of the experiments at lower temperatures.

(Signed) WALTER ROSENHAIN,

for DIRECTOR.

August 29th, 1923.

VS/569.

II. Determinations of the Viscosity of Glass.

Programme of Research,
Ref. Items 1, 2 *and* 7 (a).

PART III. (b).

Interim Report by the National Physica Laboratory on Investigations carried out on behalf of the Glass Research Association.

Summary: A method has been worked out for measuring the viscosity of glass at temperatures up to 1500° C., which depends upon determinations of the rates of fall through the glass of a platinum-iridium ball suspended on a wire of similar material from a frictionless pulley, on the opposite side of which can be placed suitable counterpoises. The apparatus has been calibrated by measuring the viscosity of "Lyle's Golden Syrup" at various temperatures. Owing to the very rapid variation of viscosity with temperature, a special furnace has been designed in which the variations of temperature are reduced to a minimum. A very accurate form of optical pyrometer has been constructed for the measurement of temperature. Satisfactory measurements of the viscosity of the glass St. 59 have been made, and the apparatus has been shown to be suitable for the determination of viscosities whose values lie between 100 and 10,000 C.G.S. units. The viscosity of glass during "fining" is within these limits.

THE problem of measuring viscosities at high temperatures has been investigated, and a method has been worked out enabling measurements to be made up to a temperature of 1500° C. For these experiments a special furnace has been designed, and with the collaboration of the Heat Department of the Laboratory, a very accurate form of optical pyrometer has been constructed for measuring the temperatures. The pyrometer, which is very simple in construction, is described in a separate report, as such an instrument should be of considerable value to the glass industry.

The viscosity is determined by measuring the rate of fall through the glass of a partially counterpoised platinum-iridium ball suspended on a platinum-iridium wire. The diameter of the ball is one centimetre, and the wire is one metre long and one millimetre in diameter. The alloy from which they are made contains 90% platinum and 10% iridium. The pots to contain the glass are made by slip casting under pressure, using a core so that the dimensions both inside and outside are reproducible. They are made of a mixture of 60% china clay, 20% sillimanite flour and 20% sillimanite passing through a sieve of 20 meshes to the inch but stopped by a sieve of 30 meshes to the inch, and are fired to Seger Cone 20 (1530° C.). The pots are 4-in. high inside and are completely filled with glass. The diameter at the top is 8.23 cms., and at the bottom 6.33 cms. The apparatus was calibrated by means of "Lyle's Golden Syrup," which was placed in a brass vessel of similar dimensions immersed in a thermostat. The calibrating vessel was slightly higher than the clay pots, and was provided with a watertight cover carrying in the centre a long brass tube through which could be passed the platinum ball and wire. In this way, the vessel could be deeply immersed in the thermostat. The top of the brass tube was covered, except for a very small opening to take the wire, and no effects due to slight evaporation of the syrup could be detected, even after prolonged experiments. The vessel, of course, was filled with syrup up to a level corresponding with the height of the clay pots. The viscosity of the syrup was measured at various temperatures by dropping steel balls of diameter 3/64 in. through a cylinder of the liquid, and measuring the rate of fall over a distance of 5.93 cms. in the middle of the cylinder. The height of liquid in the cylinder was 30 cms. and the diameter 4.7 cms. In calculating the viscosities, Ladenburg's corrections for the finite size of the vessel were applied to Stokes' formula relating to the velocity of fall of a solid sphere in an infinite quantity of viscous fluid. The measurements were made in the same thermostat and simultaneously with the measurements conducted with the large platinum ball. The results are shown in Fig. 1. The determinations at the different temperatures were made in an irregular order and it is clear from the smoothness of the curve that the viscosity of the syrup

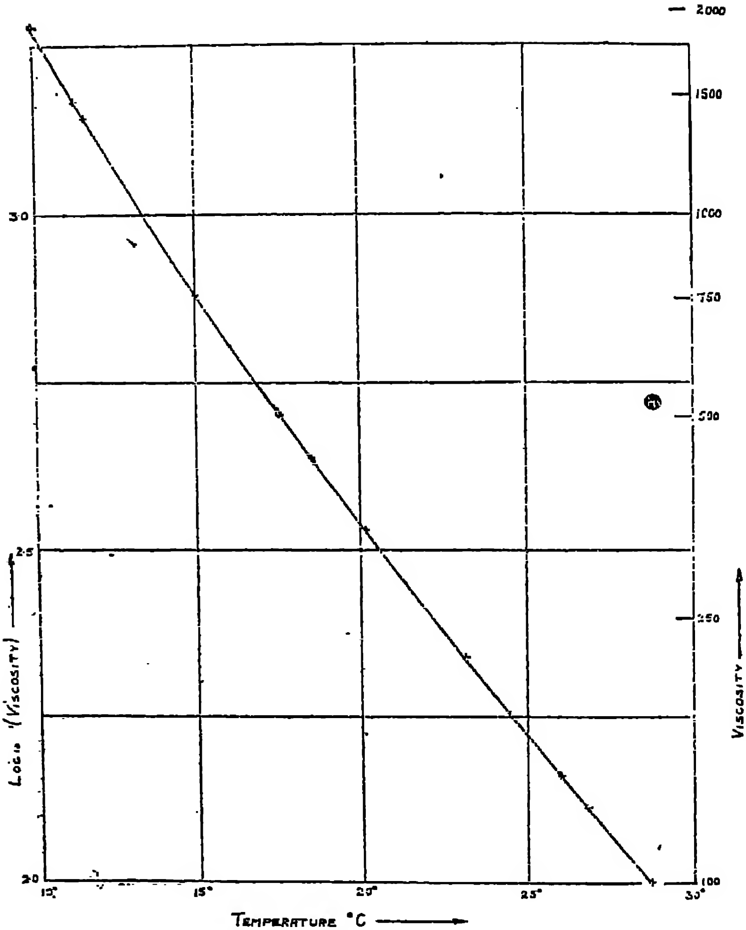


Fig. 1.

does not depend to an appreciable extent on its past thermal history within the range of temperature which was employed. The platinum ball was suspended from an extremely light form of balance, constructed in an aluminium alloy. The balance rests upon two steel balls of diameter 3/64 in. in lieu of knife edges, and turns to a milligram. Sectors concentric with the line through the centres of the balls are fitted to the arms of the balance, and over these sectors hang light threads carrying the

scale pans and the platinum ball. The variation of load due to the different positions of the threads, corresponding with different positions of the balance, is a small fraction of a milligram. The centre of gravity of the balance is adjustable and is made to lie on the line joining the centres of the balls supporting the balance. The arrangement constitutes virtually a frictionless pulley. The inertia of the balance is quite negligible

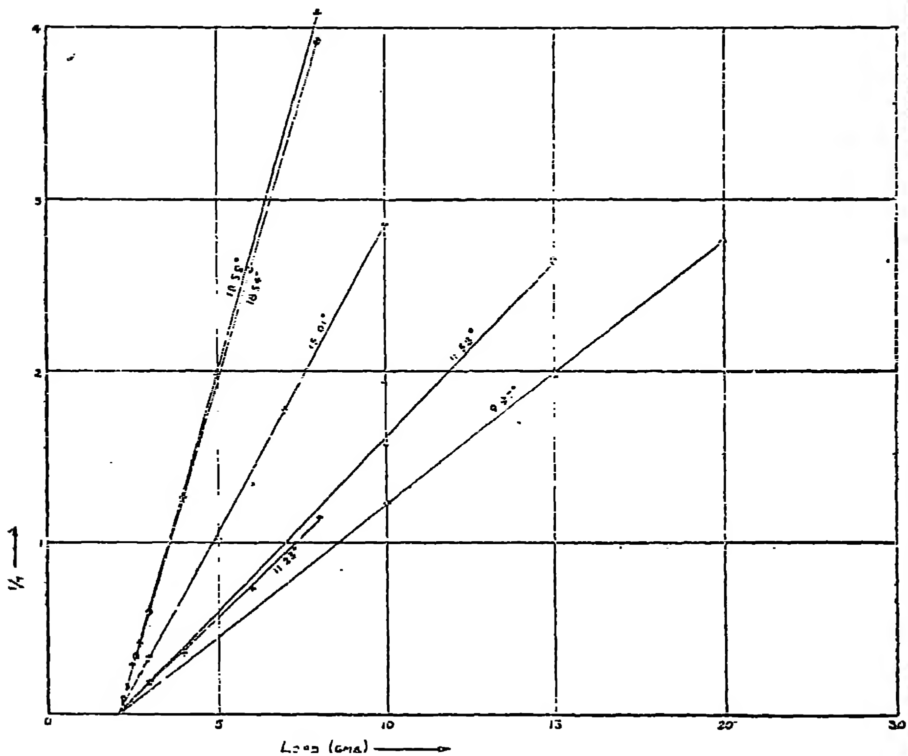


FIG. 2.

compared with that of the platinum ball, and the viscosities to be measured are so high that the inertia of the ball and its counterpoise is only of importance for an excessively short time at the beginning of the motion. This portion of the fall is not utilised in the measurements. By means of a chronograph controlled by a seconds clock (accuracy about 1/40 second),

measurements were made of the velocity-space curve of the ball, the position of the ball being measured by reading through a telescope a scale fixed to the platinum wire. The distances were measured from the position in which the ball rested on the bottom of the pot. It was found that after initial disturbances due to the inertia of the liquid the velocity of the ball diminished lineally with the depth of immersion up to a point near the

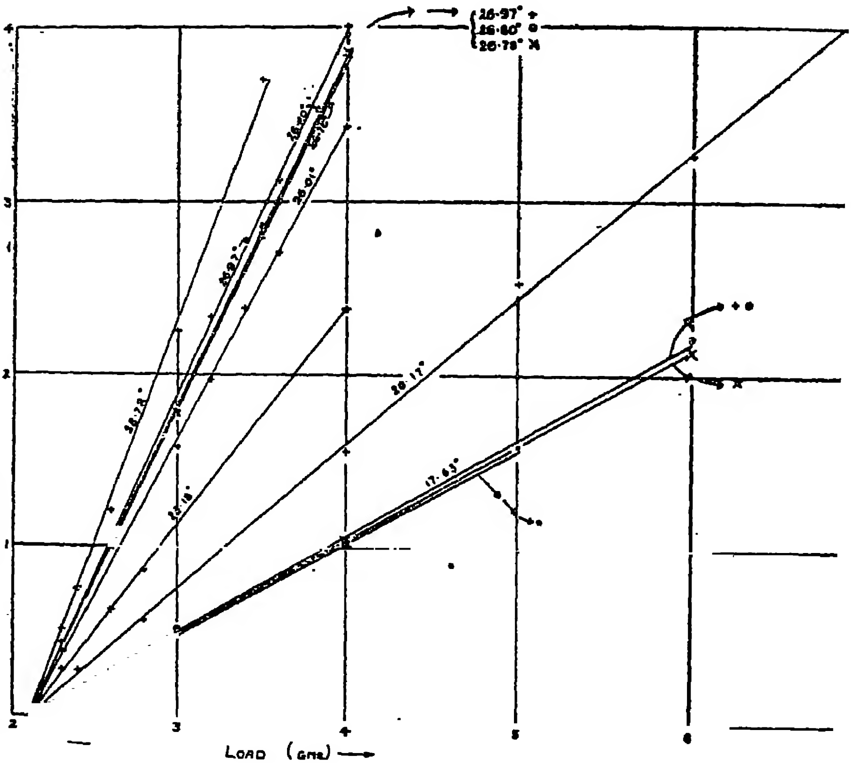


FIG. 3.

bottom of the pot. In all cases, the motion was free from initial disturbances at a point 70 m.m. from the zero position (i.e., with the ball resting on the bottom). If, however, readings were taken beyond the point 50 m.m. the agreement between different determinations began to fall off owing to the small velocity near the bottom and the effect of small errors in the zero-measurement.

Accordingly, the instrument has been calibrated in terms of the time of fall between the points 70.65 m.m. and 50.3 m.m. The method of experiment was as follows :—

The ball was first lowered to the bottom of the pot and the cross wire of the telescope set to zero. The ball was then raised by a fixed load on the other arm of the balance until the top of the ball was at the surface of the liquid. After a lapse of five minutes for drainage, the ball was allowed to fall under the action of a known load. The times of fall between the fiducial points were determined, and the reciprocals plotted against the corresponding loads (Figs. 2 and 3). Straight lines were obtained in every case and the intercept on the load axis was always 2.1 gms. On applying this load, the ball descended exactly to the second fiducial point. It may further be remarked that accurate centring of the ball in the pot was not found to be necessary. The results of the calibration are shown in Fig. 4. The " calibration factor " is the value of ηs where the slope $s = 1/tP$, t being the time of fall in seconds, and P the excess of load over the zero load. The values of the calibration factor corresponding with log η=2.645 and 2.636 appear to be quite wrong, and have been ignored in drawing the curve. The points marked with crosses in circles are probably the most reliable, being the results of the latest determinations which were made with greater precautions than the earlier points. The density of the syrup was 1.438. It may be assumed that when working with glass the value of the calibration factor to be used is that corresponding with the value of the kinematic viscosity (viscosity/density) of the syrup equal to that of the glass. It is not necessary for this purpose to use a very accurate value for the density of the glass, since multiplying the kinematic viscosity by about 32 makes a difference of only 13% to the calibration factor. It should be remarked that the admissibility of the above assumption is open to some question, such admission being equivalent to the supposition that the hydrodynamical properties of the two liquids are completely expressible in terms of the density and the viscosity, and that the results of the experiments with the platinum ball are not influenced by certain minor effects, such as phenomena connected with the draining, or the effect of the

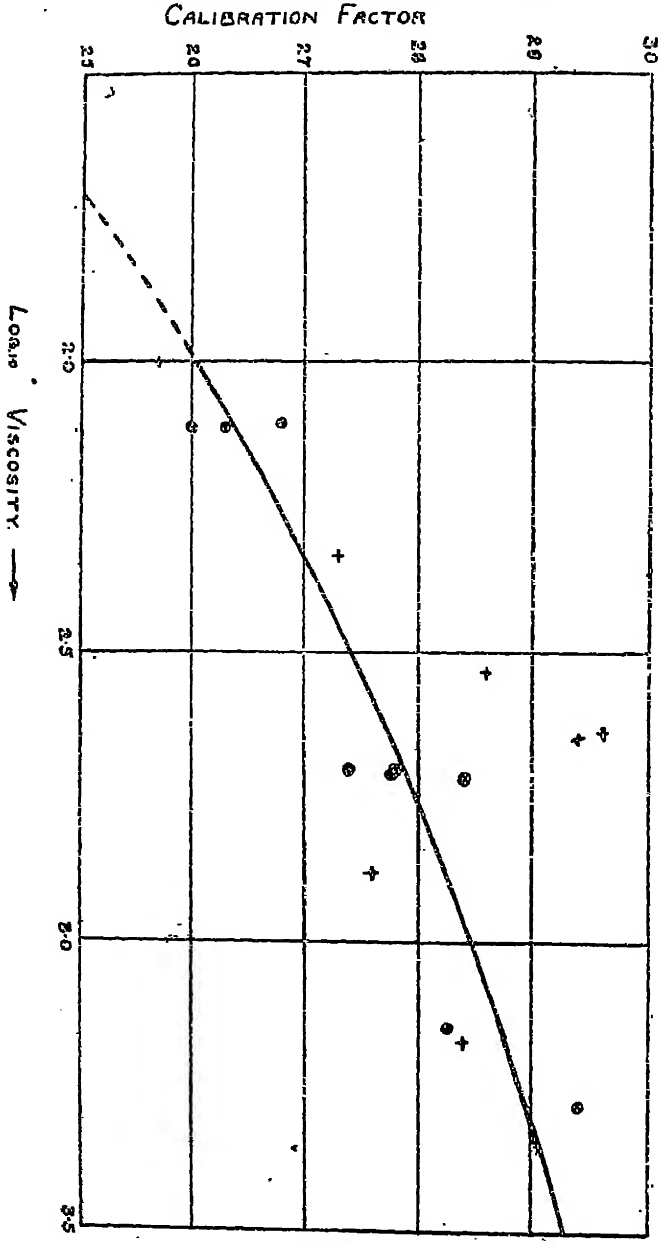

CALIBRATION FACTOR
25
26
27
28
29
30
LOG10 VISCOSITY.
2·0
2·5
3·0
3·5

FIG. 4.

inertia of the moving parts of the system other than the liquid. The direct evidence of the experiments shows that the drainage errors have been made negligible, and it has been calculated that the greatest effect due to inertia of the solid parts of the system is only 0.4% of the viscous resistance (in the extreme case of the lowest viscosity measured). The variation in the calibration factor is therefore due either to the inertia of the syrup or to the variation of its viscosity under different conditions of measurement. The truth of the former supposition would necessitate the adoption of the assumption of which the admissibility is in doubt. Additional data bearing on this question are available, although they are insufficient to settle the matter. Some work earlier than that described above was done on a method of measuring viscosity by determining the logarithmic decrement of a cylinder suspended from a torsion wire and oscillating in the liquid. Using a syrup solution similar to that employed in the later experiments a variation was found in the "calibration factor" of the same sign and approximately the same magnitude as that found in the experiments with the platinum ball. (In the logarithmic decrement experiments the variation of the "calibration factor" from $\eta=100$ to $\eta=1000$ was 10.7% of the value for $\eta=100$. In the platinum ball experiments, the corresponding value was 9.2%). The effect was at first thought to be due to the variation of the viscosity with rate of shear. It was noted that the maximum circumferential velocity of the oscillating cylinder was .028 cms. per second, whilst the velocities of the steel balls used in calibrating the syrup varied from .0060 to .074 cms. per second. It was probable, therefore, that a variation in the viscosity with rate of shear could be detected in the change of the logarithmic decrement with amplitude. No such effect could be observed. It must be remarked, however, that the effect would probably be greatest when the viscosity, and therefore the logarithmic decrement, were greatest, and in this case the variation of the latter with amplitude becomes very difficult to measure. With regard to the supposition that the variation of the "calibration factor" with viscosity is due to the inertia of the liquid, such a hypothesis seems very improbable in the case of the oscillation experiments. Fawsitt (Proc. Roy. Soc. 1908, LXXX., p. 290) has measured the

logarithmic decrements of a disc oscillating in liquids of very greatly varying viscosities and densities. If we assume that the hydrodynamical properties of the liquids can be completely expressed in terms of the density and the viscosity, and further, that the resistance to the motion of the disc can be expressed as the sum of a couple proportional to its acceleration, and a couple proportional to its velocity, it may be shown by a consideration of the dimensions of the quantities involved, that, for the same apparatus, λ/η is a function of ρ/η where λ is the logarithmic decrement of the disc, η the viscosity of the liquid and ρ its density. The curves of Figs. 5 and 6 which contain the points used by Fawsitt for calibration show that this is the case. It

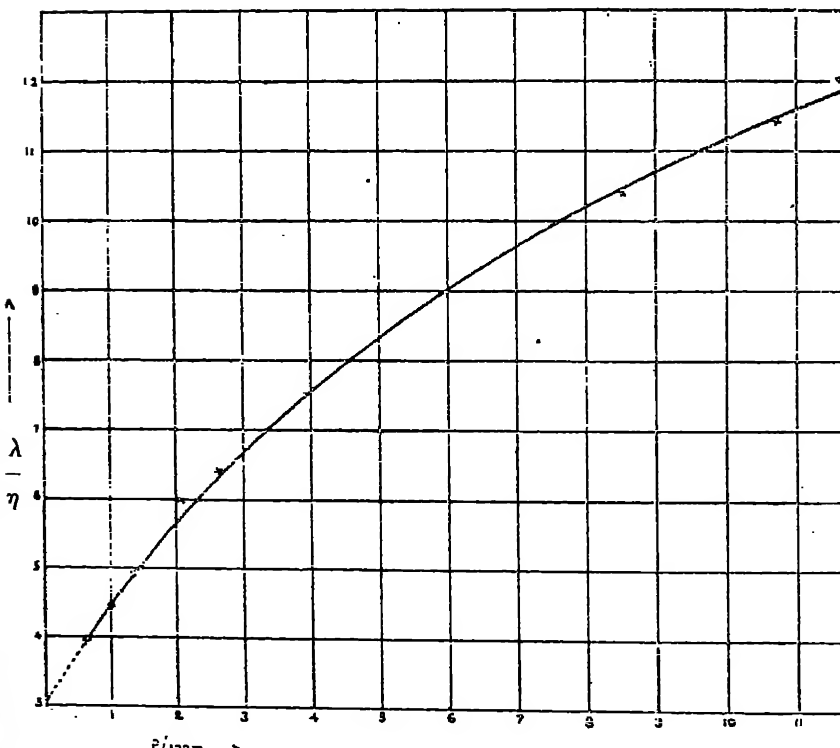


FIG. 5.

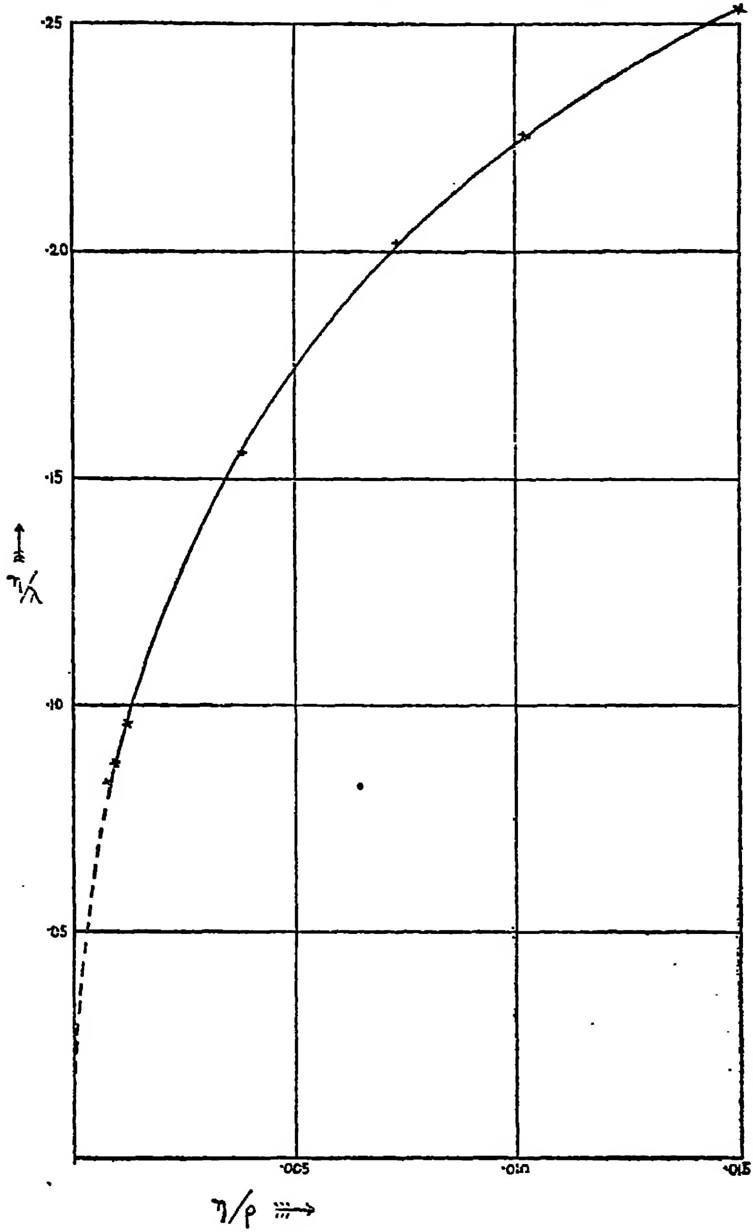


FIG. 6.

will be observed that for large values of η the value of λ/η approaches a limit, and that for a value of ρ/η corresponding with $\rho=1.43$ and $\eta=100$ (i.e., the lowest value of η used in our experiments), the value of λ/η is within one ten thousandth part of its limiting value. Since the dimensions of our oscillating system did not differ very greatly from that used by Fawsitt,

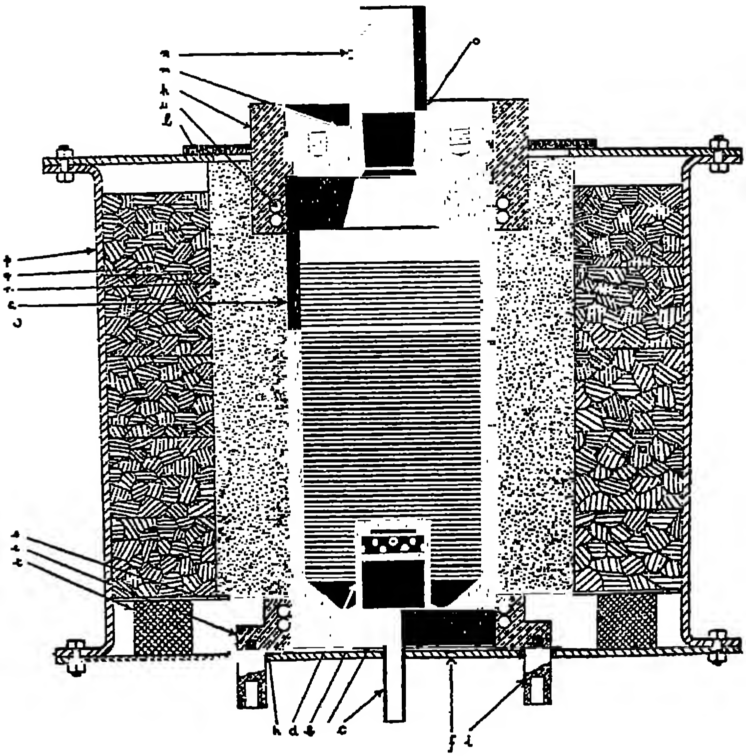


FIG. 7.

these considerations suggest very strongly that the variation in the value of λ/η is not merely the inertia effect of the liquid. It would seem, then, that in spite of failure to observe a variation of the logarithmic decrement with amplitude, it is probable that the viscosity of syrup does depend on the rate of shear. At the

present time the above discussion may appear to be of academic rather than of practical interest, but it must be remembered that the interpretation of experiments on the viscous properties of glass is by no means a simple matter, and it is not desirable unnecessarily to increase the inherent difficulties by the introduction of unknown properties of other liquids used for calibration. There is one more point which may be mentioned in this connection. It might be supposed that the variation of the viscosity of syrup with the rate of shear, if it exists, could be measured by dropping through the liquid small spheres of varying sizes. Such experiments would not give the desired information because the effect to be observed would not be of greater magnitude than the uncertainty of the corrections for the finite size of the containing vessel, which would have to be applied in the case of the larger balls.

It will readily be appreciated, that owing to the great variation of the viscosity of glass with temperature, a very carefully designed furnace and accurate means of measuring the temperature are necessary. The furnace which has been constructed is similar in principle to that described by Rosenhain and Coad Pryor in the Transactions of the Faraday Society, Vol. XIV., part 3. A diagram of the original furnace is shown in Fig. 7. The main features of the new design are shown in Fig. 8. The heating elements, as before, consist of a number of graphite rings arranged in a pile so as to form a tube. To increase the stability of the pile, the rings are cut at an angle of 30° with the horizontal. Rings with horizontal surfaces may, however, be used satisfactorily. The lower portion of the furnace is conical so as to reduce the heat losses at the end, and all the rings offer the same area to the passage of the current. In this furnace, this arrangement results in very uniform heating, but adjustments of the design might be necessary for a furnace of different dimensions. A block in the shape of an inverted cone is fixed to the bottom of the furnace and serves to support a cylindrical muffle. (The muffle is shown in Fig. 9). The first block and stem were made in one piece out of a mixture of 60% carborundum and 40% china clay and the stem was fixed into a sheath at the bottom of the furnace by means of Portland

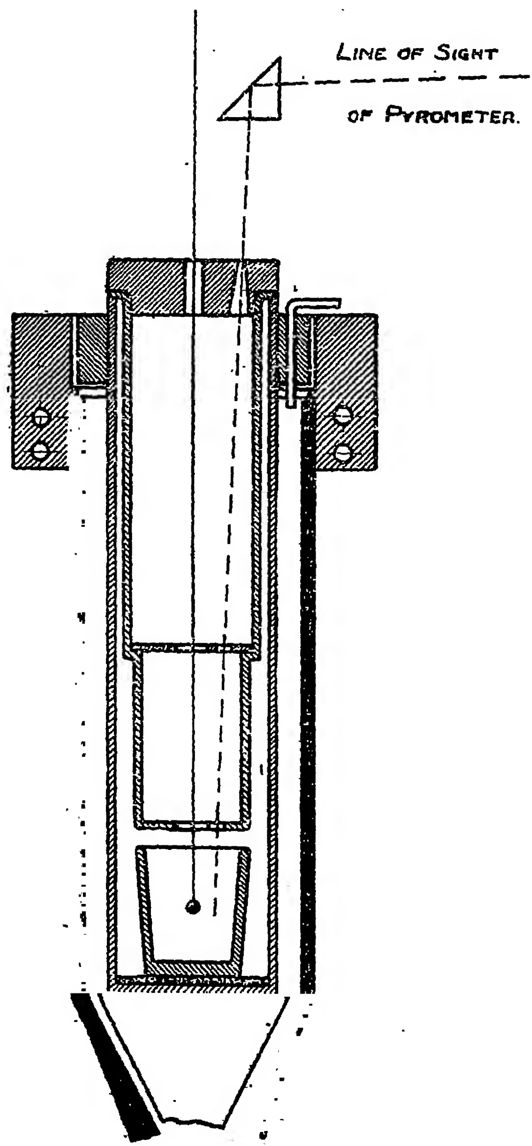


FIG. 9.

cement. The arrangement proved satisfactory, but the carborundum was later replaced by graphite which lessens the danger of damage through accidental over-heating. The muffle, which is made by slip casting, contains 60% carborundum and 40% china clay, and is fired to Cone 26 (1560° C.). This temperature is high enough to produce thorough vitrification of the bond which is very necessary in the case of a muffle used in a graphite furnace, owing to the tendency of reducing gases and even carbon particles to penetrate the walls of the muffle. The joint between the muffle and the upper electrode is made with a mixture of clay, carborundum, and sodium silicate. This cement sets hard in the cold and the shrinkage is sufficient to allow the muffle to move freely with respect to the electrode. It is necessary to put a plentiful supply of vaseline on the electrode before applying the cement in order to prevent corrosion of the aluminium and subsequent sticking of the muffle to the electrode. When performing an experiment, the pot is placed in the centre of the muffle on a layer of sand. Above the pot is lowered a second muffle of china clay, which is suspended from the top edge of the main muffle by means of a flange. The bottom of the china clay muffle is about ½ in. above the top of the pot. A horizontal disc of china clay is supported on a flange inside the china clay muffle 6 in. above the bottom. This disc, and also the bottom of the china clay muffle are provided with central holes 1 in. in diameter to allow the passage of the platinum ball, and a ½ in. diameter hole is also provided in each through which the optical pyrometer is sighted. The normal line of sight of the latter passes through the centre of the pot at the bottom, and about half-way between the centre of the pot and the outside at the top. It has been found that the enclosure between the bottom of the carborundum muffle and the bottom of the china clay muffle behaves as a perfect black body. On sighting the optical pyrometer on a pot of glass, no difference in temperature could be detected between the centre of the pot and a point 1 in. away from the centre. As the radius of the pot used in the measurements is only 1½ in., the temperature measurements may be considered accurate within the limits of error of the pyrometer itself.

With regard to the measurements of viscosity, the general method of experiment has already been outlined. Certain precautions, however, remain to be mentioned. Care must be taken to prevent the platinum wire from fouling the apertures in the baffles through which it passes. For this reason, it has been found desirable to make the necessary adjustments before starting up the furnace, so that no adjustments need be made afterwards. This means that the whole of the charge of glass

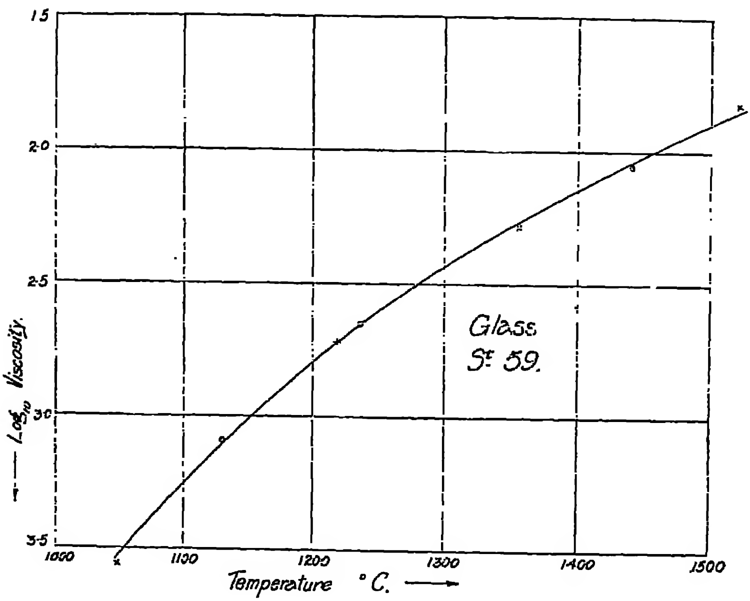


FIG. 10.

must be in the pot at the beginning of the experiment when the furnace is cold. It is necessary, therefore, to prepare the charge of glass by first casting a piece of the glass of the same volume as that of the pot, but slightly smaller in diameter, so as to allow for expansion, and also because the pot may be slightly warped. The piece of glass is cast in an iron mould and allowed to cool in a large furnace similar to the glass-melting furnace previously described.

To increase the life of the carbon parts of the furnace, a current of nitrogen is passed into it. It is usual to lead the gas in at the top of the furnace and out at the bottom, but owing to the large height of this furnace, it is not possible in this way to maintain a pressure of nitrogen sufficient to prevent ingress of air at the bottom, and it is necessary to bring in the nitrogen through the pipe originally designed for its exit. The exhaust pipe is therefore now at the top of the furnace. The experiments must be conducted in a well-ventilated room, and a current

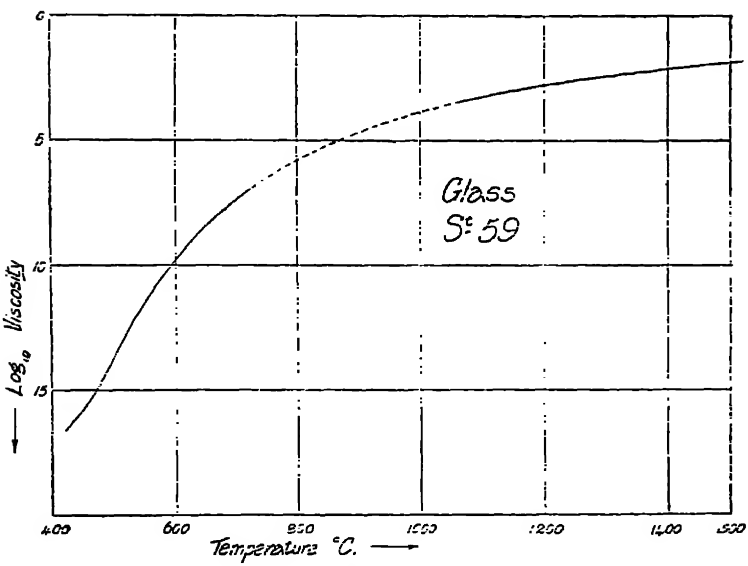


FIG. 11.

of air from a fan must pass continually over the furnace. It is not necessary to stop the fan even when using the balance. Owing to the heat capacity of the conical block which supports the muffle, the furnace does not respond readily to small fluctuations of the power input, and the temperature can easily be maintained constant to within two or three degrees for an hour or two. After making a measurement about two hours must elapse before a measurement can be made at a new temperature. It has already been explained that at the beginning

of a measurement the ball is lowered to the bottom of the pot in order to set the telescope in its proper position. When working on glass, this operation is only done once at the beginning of the series of measurements in order to avoid stirring up the viscous layer of glass at the bottom of the pot. When pulling up the ball by hand, it is quite easy to feel the very much increased resistance experienced when the ball is at the bottom of the pot. After the telescope has been adjusted a stop in the balance case is used which arrests the balance when the ball has just passed the second fiducial mark. The necessity for using a ball made of a material which is not attacked by glass is manifest, and it is clear that, in general, methods for measuring the viscosity of glass at high temperatures in which ordinary refractories are employed for *all* the parts, can be satisfactory only when the apparatus is of considerable size.

The results of some measurements which have been made on glass St. 59 are shown in Figs. 10 and 11. Viscosities of rather less than 10^2 C.G.S. units can conveniently be measured, and at the other end of the scale earlier experiments conducted with a different furnace showed that viscosities of about 10^4 C.G.S. units are not too high for convenient measurement. The other methods of measurement which have been described can be used between viscosities of 10^7 and $10^{16.6}$ C.G.S. units, which leaves a gap having a ratio between its extreme values of about 10^3. As the ratio of the extreme values measured is nearly 10^{15}, this gap is relatively small. It is probable, moreover, that measurements within this range would be difficult to perform on many glasses owing to devitrification.

(Signed) WALTER ROSENHAIN,

August 29th, 1923. for DIRECTOR.

VS/569.

III. Determinations of the Viscosity of Glass.

Programme of Research,
Ref.: Items 1, 2, and 7(a).

PART III. (c).

AN OPTICAL PYROMETER FOR ACCURATE TEMPERATURE MEASUREMENTS.

Interim Report by the National Physical Laboratory on Investigations carried out on behalf of the Glass Research Association.

THE pyrometer, which has been designed for use in connection with the viscosity measurements at high temperatures, is of the disappearing filament type, and is capable of a high degree of accuracy. As such accuracy is not yet attainable in commercial pyrometers of this type, it will be useful to indicate the principles underlying its design. As is well known, a real image of the hot object is formed in the plane of a small lamp filament by means of a lens. This image and the lamp filament are viewed through a magnifying system, and also through a suitable coloured glass, and by varying the current through the lamp the brightness of a definite portion of the filament is rendered equal to that of the background. Equality of brightness is recognised by the complete or almost complete disappearance of the section of filament utilised. (The filaments used for this purpose usually have a loop arranged for convenience in picking out a definite portion.) It has been found that the accuracy of the instrument may be increased by viewing the filament through a system of high magnifying power. The highest accuracy cannot, however, be obtained merely by increase in the magnification. Owing to the effects of diffraction, dark or light bands are formed near the edges of the filament and prevent its complete disappearance. These bands may be eliminated by the use of a diaphragm with a small aperture in the eye-piece, wihch diminishes the resolving power of the

system so that the diffraction bands cannot be seen. If the aperture of the diaphragm is extremely minute, the filament disappears against the background so readily that a considerable change in the current is necessary to cause its re-appearance, and the sensitivity of the instrument is poor. It will be clear, then that the highest sensitivity is to be attained by the use of the largest aperture, which is at the same time small enough to cause disappearance of the diffraction bands, the least trace of which greatly lowers the accuracy of the setting. The best size of aperture depends on many factors, including the thickness of the filament, and must be determined by trial. The instrument which has been constructed in the Laboratory is shown in Fig. 1. The objective has a focal length of 150 m.m. and forms an image in the plane of the filament. The lamp is mounted in such a way that it may be rotated about its own vertical axis of symmetry, and about a parallel axis at a distance of 5 m.m. from the former, and can also move vertically upwards or downwards. These movements are provided in order that a new lamp may be adjusted so that its filament is in the correct position with respect to the optical parts of the instrument; the moving parts can be locked after the adjustment has been made. The viewing system consists virtually of an astronomical telescope having an objective of focal length 50 m.m. at a distance from the lamp of approximately twice its focal length, and a Huyghens occular giving a magnification of 15 diameters. The diaphragm with an aperture of 1 m.m. is placed between the occular and the objective of the viewing system at a distance from the latter equal to its focal length. By the rotation of a sleeve on the tube, the aperture in the diaphragm can be changed to one of 4 m.m. diameter and the instrument can then be used at the lowest temperatures at which visible radiation is emitted. It is readily seen from considerations of geometrical optics that the brightness match is independent of the distance of the pyrometer from the object. Owing, however, to the phenomenon of diffraction, variation in the size of the aperture limiting the angle of the cone of light used has a small influence on the matching apart from the question of sensitivity. For the same reason it is necessary that the angle of the cone of light which forms the first image of the hot object in the plane of the filament should not vary

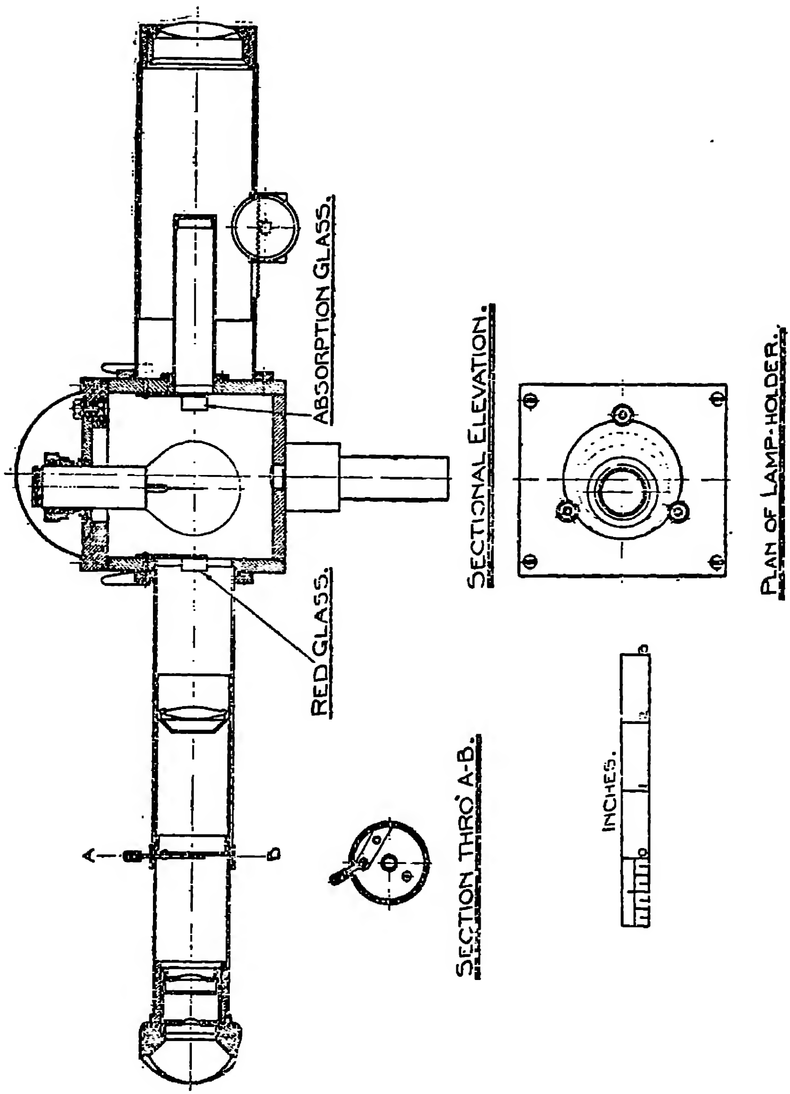

ABSORPTION GLASS.
RED GLASS.
SECTIONAL ELEVATION.
PLAN OF LAMP-HOLDER.
SECTION THRO' A-B.
INCHES.
A
B

Fig. 1.

in value with a change in the distance of the object. This result is achieved by means of a diaphragm at a fixed distance from the lamp. The field of view of the instrument is limited by the diaphragm in the occular and is approximately 4°. It may be noted that the final image of the furnace is erect, this being a point of considerable practical importance. Between the lamp and the eyepiece the instrument is fitted with a red absorption glass 5 m.m thick known as "Corning high transmission red 150%." By the rotation of a small lever the glass may be put out of action when the instrument is used at very low temperatures. A second absorption glass similarly mounted is fitted on the opposite side of the lamp for use at temperatures exceeding 1500° C. The lamp itself is of the pattern used in the Leeds and Northrupp instrument. The instrument is calibrated by observations of a black body furnace maintained at the temperature of melting palladium, the lower temperatures being obtained by the use of suitable rotating sectors. It may be shown from Wien's law that if λ be the effective wave length of the light transmitted by the red glass, T_1, the absolute temperature of the black body furnace, and T_2 the absolute temperature of the black body which has the same brightness when viewed directly through the red screen as the furnace when viewed through the same red screen and also through a rotating sector of fractional transmission R,

$$1/T_1 - 1/T_2 = \lambda \log_e R/C_2$$ where C_2 is a constant.

The above equation may be written

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{\lambda \log_{10} R}{C_2 \quad \log_{10} e}$$

C_2 is assumed to have the value 14350 μ °C. and therefore

$$C_2 \log e = 6232 \ \mu \ °C.$$

The melting point of the palladium is taken as 1828° K (1555° C.). The calibration curve of the instrument could be recalculated and results corrected at any future date if these constants were found to require revision.

The value of λ varies slightly with temperature and may be obtained by comparison with a known glass of similar composition. It may also be measured, slightly less accurately, by means of observations of a black body at the temperature of melting gold, which is assumed to be 1336° K. (1063° C). In either case the change of λ with temperature is known to be the same as that of red glasses of similar composition. (See Forsythe, Trans. Far. Soc. Vol. XV., part 3. June, 1920.) For work at temperatures above 1500° C. an absorption glass is used between the furnace and the lamp. This glass is calibrated by comparison with rotating sectors. Messrs. Leeds and Northrupp use for this purpose an absorption glass which compensates for the change in λ with temperature of the Corning red glass in such a way that the calibration need only be made at one temperature, the effect of the absorption glass being to subtract a constant quantity from the reciprocal of the apparent absolute temperature. The use of this glass, whilst convenient, is by no means essential.

The accuracy of the pryometer depends chiefly upon the constancy of the lamp and upon the eye of the observer. With regard to the former, Forsythe quotes a specially favourable case of a lamp which was used almost daily for two years at temperatures mainly in the region of the melting point of palladium. Altogether the lamp was used for 300 hours and its calibration at 1555° C. was found to have changed less than 1½° C.

With respect to the eye of the operator, the mean of six readings of a steady temperature should be repeated by the same observer to plus or minus one or two degrees at temperatures between 1000° C. and 1500° C. So long as the Corning red glass is used the differences between different observers are less than this, even though the visibility curves for the different eyes may vary very considerably. These statements apply to skilled observers, but inexperienced observers are usually accurate to within three degrees. It may be remarked that if black body conditions are satisfactorily obtained, this type of pyrometer, whilst less sensitive than a thermocouple, is more accurate when absolute

values of the temperature are required (except when the thermocouple is used under precisely the same conditions as those obtaining during the calibration). The calibration of the optical pyrometer requires checking at much less frequent intervals of time than that of a thermocouple used at the same temperatures.

When used in connection with the viscosity measurements, the pyrometer is used in conjunction with a 45° glass prism in order that the pyrometer may be used in a horizontal position. The use of the prism involves a correction to the temperature of from 19° to 38° at temperatures between 1000° C. and 1500° C. This correction is readily determined at a single temperature by taking observations of a black body with and without the mirror, and from the correction at one temperature the correction at other temperatures can be calculated.

(Signed) Walter Rosenhain,
for Director.

August 29th, 1923.
VS/569.

IV. The Electrical Conductivity of Glasses.

Programme of Research.
Item 6.

Abstract: The electrical conductivity has been measured of various glasses at temperatures varying from about 600°C to about 1150°C. The method of making the measurements is described and results are given showing the variation of conductivity within that range of temperature for series of glasses including soda silicates, soda magnesia, soda alumina and soda lime silicates. The possibility of using conductivity measurements for obtaining a measure of the variation in the viscosity of molten glass as it flows from a tank is suggested and a method is described for obtaining such measurements.

Introductory.

THE electrical properties of glass have been studied by various investigators who have measured the insulation resistance, the dielectric strength, and the specific inductive capacity of various types of glasses. These properties have attracted attention because of the many uses of glass as an insulating material. Glass is also, to a certain extent, a conductor of electricity and the nature of the conduction process has at different times been investigated. That the conduction of electricity through glass is of an electrolytic nature was first pointed out by Warburg in 1884, who showed that the passage of the electric current through glass is due to the motion of the sodium in the glass. His experiments were repeated in 1910 by Le Blanc and Kerschbaum, who came to the conclusion that conduction was entirely due to the motion of the sodium present in the glass and that at a temperature of about 250° C. the glass is ionised to an extent of about 80%. They also observed the formation of a poorly-conducting layer at the anode when mercury electrodes were used, and showed that if a sodium amalgam were employed as anode the layer was not formed, the sodium from the amalgam replacing that removed from the glass under the influence of the current. The work has been developed by later investigators, and it has been shown that it is possible to electrolyse certain metals through glass, using as electrodes

amalgams of the metals or fused salts. The appearance of the glass after such a process is generally completely changed. In some cases the glass becomes porous and milky white, in other cases pronounced colour effects are produced, which may be attributed to a colloidal condition of the metal. Fig. 1 shows the appearance under slight magnification of a soda lime glass tube 9.5 mm. in external diameter, with a bulb blown at the end, through which a current has been passed from a copper amalgam anode outside to mercury inside the tube, the glass being maintained at a temperature of about 300° C. The tube has become a brownish colour, which is not quite uniformly distributed but is concentrated in small patches over the surface. Fig. 2 is a photograph, magnification 80, of a small area on the surface of the bulb showing the cell-like appearance of these patches. If the tube be heated, the colour changes to light blue and the glass becomes full of bubbles of gas absorbed during the process of electrolysis. More recent work on this subject is detailed in a paper by Kraus and Darby (Journ. Amer. Chem. Soc. 44, 12, Dec. 1922), who have studied the replacement of the sodium contained in glass by other metals.

Conductivity at Higher Temperatures.

Very little work has previously been done on the conductivity of glasses at temperatures above their softening point, and as information on the subject seemed desirable measurements were made of the variation of conductivity as the temperature increased from above the softening point to the working temperature.

Preliminary observations showed that at these temperatures conductivity is largely of an electrolytic nature. When an electromotive force is imposed on electrodes immersed in molten glass, the current which passes through the glass between the electrodes rapidly diminishes during the first minute or so and thereafter more gradually until something approaching a steady state is reached. As the current passes, a number of bubbles of gas form round the positive electrode, the number and size of these depending on the quantity of

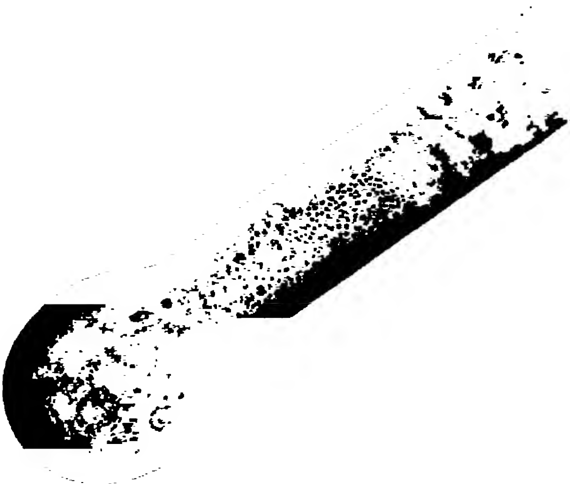


Fig. 1.

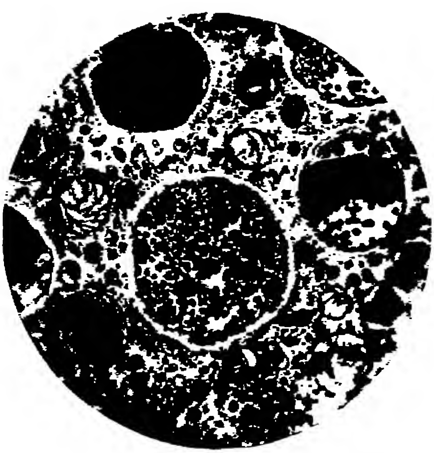


Fig. 2.

electricity that has passed. These bubbles are one of the products of electrolysis and as they form they gradually surround the electrode thus partly insulating it, and this partial insulation together with the absorption of a certain amount of the gas by the electrode causes the diminution of the current. On account of the viscosity of the glass the bubbles cannot readily escape, but there is always a certain amount of movement of the glass which prevents the electrodes becoming completely insulated. This partial insulation occurs at one electrode only. If the direction of the current be reversed the current which at first passes approaches in value that of the initial current in the opposite direction. The current then falls off as before on account of the polarisation of the second electrode. If the potential of the applied electromotive force be raised there is a momentary increase in the current through the glass, followed by a more gradual decline. A similar effect is obtained if, after cutting off the current, the temperature be raised and the current again switched on.

The back electromotive force due to polarisation can be observed by connecting the electrodes to a voltmeter immediately after breaking the battery circuit. This polarisation electromotive force varies with different glasses, as does also the time taken for it to discharge through a given resistance.

If alternating current is used instead of direct current the polarisation effects are considerably reduced. The formation of gas bubbles round the electrodes is not so pronounced and consequently the rate of diminution of the current is much less. If the initial current density is sufficiently great the temperature of the glass rises as a result of the heating effect of the current. The conductivity is thus raised and the current increases. When platinum electrodes are used the passage of the current is accompanied by a continuous succession of minute flashes in the neighbourhood of the electrodes. If the platinum wire electrodes are separated by a few millimetres of glass the flashes can easily be observed when the temperature of the glass is about 700° C.

and the applied voltage about 60, or at even lower temperatures with increased voltage. The flashes are probably due to the current arcing across the film of gas or insulating material which is formed round the electrodes. As a result of this arcing the electrodes become disintegrated and the platinum is deposited in very fine particles. These go into suspension in the glass, which becomes dark in colour in the neighbourhood of the electrodes. The arcing raises the temperature of the electrodes to such an extent that they fuse.

With graphite electrodes no arcing can be observed even with voltages up to 100 and at temperatures higher than that mentioned above, but large bubbles form round both electrodes. When silver electrodes are used neither the arcing nor the formation of bubbles is observed. There is, however, a certain disintegration of the electrodes, but the penetration of the metal into the glass is not so deep as in the case of platinum. The increase of temperature due to passage of the current is not so much confined to the neighbourhood of the electrode, the temperature gradient from the electrodes to the centre of the mass of the glass not being so great and the glass between the electrodes becomes more uniformly heated. The heating continues till the electrodes fuse.

Method of Measuring the Current.

The variation of conductivity with temperature has been measured for several series of glasses. In order to get rid, to some extent, of the effects of polarisation, alternating current of a low current density has been used.

The crucibles used were about 12 millimetres in diameter by about 60 millimetres deep, and just fit inside a platinum-wound tube furnace. To hold the electrodes at a definite distance apart and at a definite depth of immersion in the glass, fire-clay tubes with double bore about three millimetres apart were used. The platinum wires used as electrodes were cemented into this tube and the exposed portions made exactly five millimetres long and three millimetres apart. The tube carrying the electrodes was passed through the bottom

of the crucible into which it was then cemented. The glass was then dropped on to the electrodes and allowed to melt, sufficient glass being added in each case to completely cover the electrodes.

The current through the glass was measured by measuring the potential drop across a standard resistance in series with the glass under observation. The appended diagram (Fig. 3) shows the general arrangement. B is a 4-volt

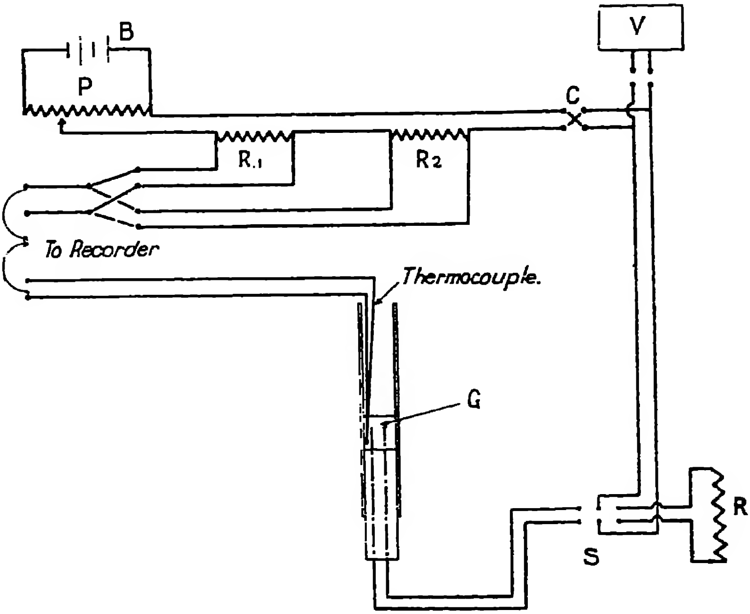


FIG. 3.

battery connected to a potentiometer resistance P. From this resistance the current is led through the standard resistances R_1 and R_2 of 1 ohm and ·1 ohm respectively. Either of these can be connected to one circuit of a double thread recorder. The commutator C reverses the direction of the current giving about 500 alternations per minute. By means of the double-pole double-throw switch S the current from the commutator can be directed either to the electrodes in the glass G or through a constant resistance R.

The resistance R is comparable in magnitude with that of the glass and is used to check, from time to time, the voltage on the a.c. side of the commutator. The temperature is measured by means of a platinum platinum – rhodium thermocouple immersed in the glass and connected to the second circuit of the recorder.

With the switch S open, the potentiometer resistance P is adjusted so that a voltage of 2 is obtained on the voltmeter V which is connected on the a.c. side of the commutator. When the recorder has made an impression giving the temperature reading, the switch S is closed in one direction, say towards R, the resistance R_1 being connected across the recorder and a reading obtained of the current through R. The next marking on the recorder chart represents temperature, and the switch is then closed so as to send the current through the glass. This procedure is continued, readings being obtained at half-minute intervals in the order, temperature, current through constant resistance, temperature, current through glass, until the current through the glass becomes too great to be recorded on the chart. The recorder is then connected across the smaller standard resistance and the readings continued.

Glasses Examined.

The following results have been obtained by the method indicated. They are put forward mainly as a preliminary survey. Further work is necessary to ascertain definitely what polarisation effects may be introduced, and to check the results by other methods. In the case of some glasses it was not possible to measure all the members of a series on account of devitrification or other changes taking place in the glass during the test, as a result of which the nature of the conduction is altered and the readings are not then comparable with those obtained at temperatures which do not produce devitrification.

The glasses were melted in experimental sillimanite pots, six inches in diameter, in a recuperative gas furnace. On account of the partial solution of the pot in the glass and also on

account of the introduction of parts of the disintegrated tiles from the top of the furnace the glasses were not pure and not quite of the prescribed compositions.

SERIES G.1.

This is a simple soda silicate of the formula

$$100\ SiO_2\ x\ Na_2O.$$

The following table gives the calculated molecular composition of the glasses :—

	A.	B.	C.	D.	E.	F.
SiO_2	100	100	100	100	100	100
Na_2O	20	30	40	50	60	70

The analyses of the resulting glasses were as follows :—

	G.1.A.	G.1.B.	G.1.C.	G.1.D.	G.1.E.	G.1.F.
Silica (SiO_2)	82·38	77·57	72·95	65·69	61·47	58·87
Iron Oxide (Fe_2O_3) ...	·11	·17	·17	·25	·14	·24
Alumina (Al_2O_3) ...	·67	·38	·63	1·45	2·05	2·09
Soda (Na_2O)	16·40	21·89	26·21	31·64	36·29	38·83
Magnesia (MgO) ...	—	—	—	·58	·43	·50
Total ...	99·56	100·01	99·96	99·61	100·38	100·53

These give the following actual molecular compositions :—

	G.1.A.	G.1.B.	G.1.C.	G.1.D.	G.1.E.	G.1.F.
SiO_2 ...	100	100	100	100	100	100
Na_2O ...	19·36	27·45	34·94	46·85	57·41	63·31
Fe_2O_3 ...	·01594	·08273	·08798	·1436	·08598	·1539
Al_2O_3 ...	·4798	·2890	·5094	1·302	1·967	2·094
MgO ...	—	—	—	1·320	1·046	1·271

Fig. 4 gives the temperature-conductivity curves for glasses G.1. B., C., D., E. and F. Glass G.1.A. was not tested because there was a considerable silica separation which would have rendered any tests unreliable. The curves show a rapid rise of conductivity, especially at the higher temperatures, with increasing soda. The curve for G.1.D. seems slightly high ; this is probably due to the proportion of MgO present as will be seen from the analyses.

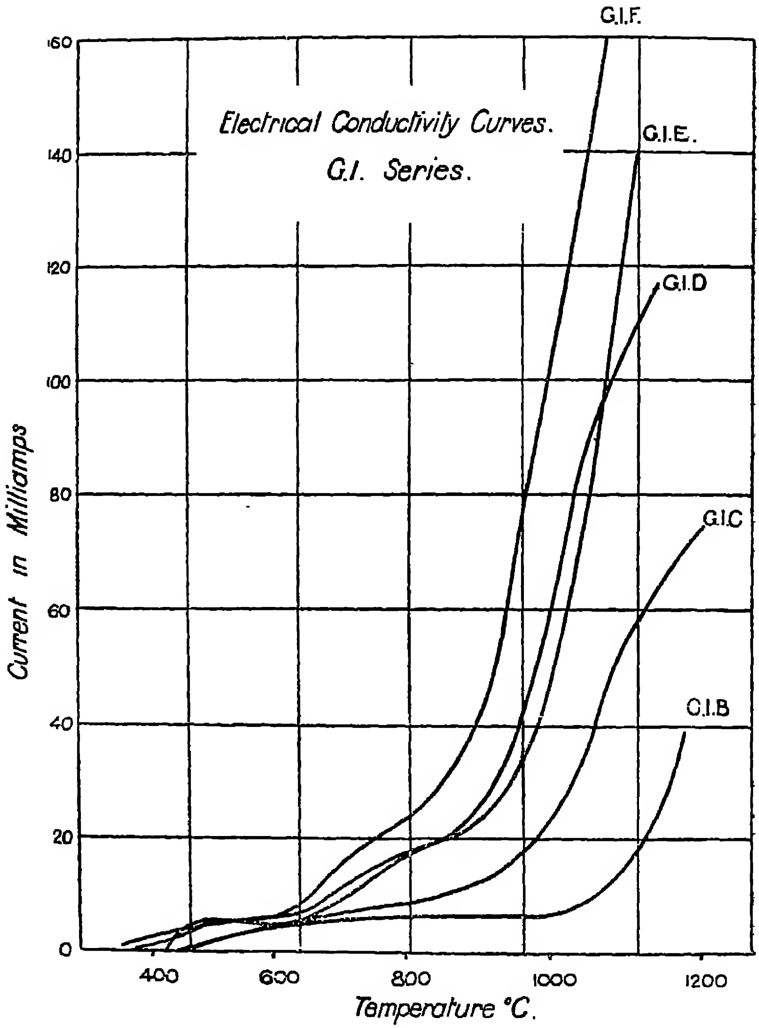

Electrical Conductivity Curves.
G.I. Series.
G.I.F.
G.I.E.
G.I.D
G.I.C
G.I.B
160
140
120
100
80
60
40
20
0
400
600
800
1000
1200
Current in Milliamps
Temperature °C.

FIG. 4.

SERIES G.2.

Formula 100 SiO_2 20 Na_2O x MgO.

Calculated molecular composition :—

	A.	B.	C.	D.
SiO_2	100	100	100	100
Na_2O	20	20	20	20
MgO	5	10	15	20

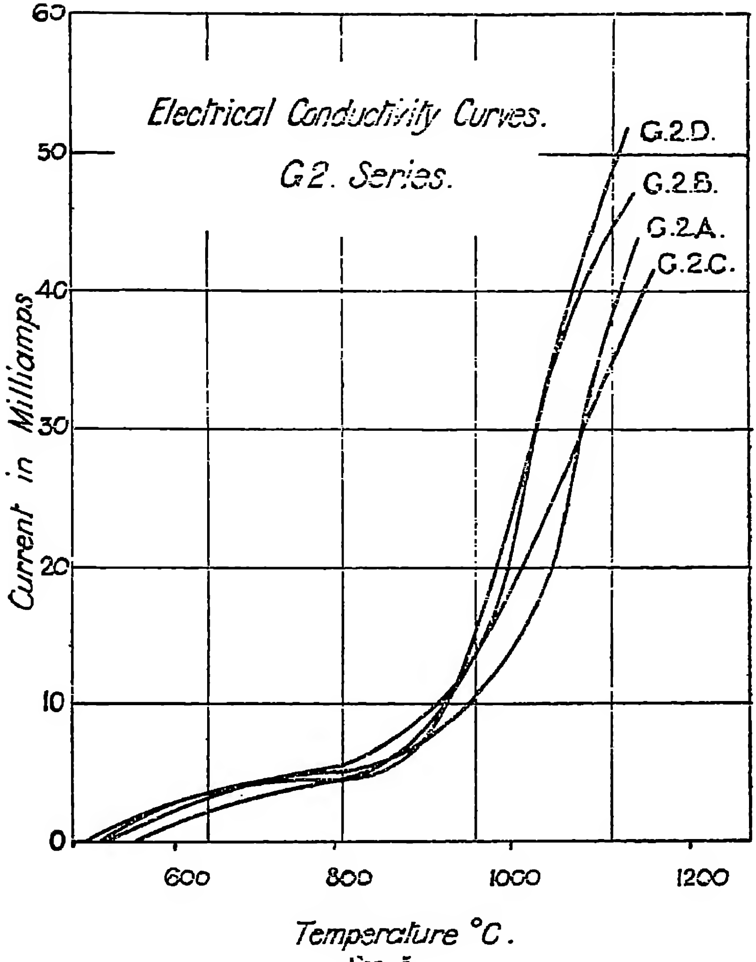


FIG. 5.

Analyses of Glasses.

	G.2.A.	G.2.B.	G.2.C.	G.2.D
Silica (SiO_2)	80·05	78·15	75·95	74·60
Iron Oxide (Fe_2O_3) ...	·085	·080	·080	·070
Alumina (Al_2O_3)	·57	·97	1·27	·83
Lime (CaO)	—	—	·50	—
Magnesia (MgO)	2·70	4·97	6·49	8·76
Soda (Na_2O)	16·23	15·99	15·38	15·25
Total ...	99·635	100·16	99·67	99·51

Molecular Composition.

	G.2.A.	G.2.B.	G.2.C.	G.2.D.
SiO_2	100·0	100·0	100·0	100·0
Fe_2O_3	·0399	·0386	·0397	·0354
Al_2O_3	·4201	·7321	·9865	·6564
CaO	—	—	·7081	—
MgO	5·0210	9·51	12·69	17·56
Na_2O	19·67	19·90	19·70	19·87

Fig. 5 gives the temperature-conductivity curves for the glasses G.2 series, from which it will be seen that at the higher temperatures increasing conductivity results from increasing MgO content. Curve C is low, probably on account of the presence of an appreciable quantity of CaO accidentally introduced.

Series G.4.

Formula 100 SiO_2 20 Na_2O x Al_2O_3.

Calculated molecular composition :—

	A.	B.	C.	D.	E.	F.
SiO_2 ...	100	100	100	100	100	100
Na_2O ...	20	20	20	20	20	20
Al_2O_3 ...	6	8	9	10	11	12

Analyses of Glasses.

	G.4.B.	G.4.C.	G.4.D.	G.4.E.	G.4.F.
Silica (SiO_2) ...	74·30	72·60	73·05	72·30	71·40
Iron Oxide (Fe_2O_3)...	·14	·21	·14	·20	·14
Alumina (Al_2O_3) ...	10·51	10·89	12·01	12·90	14·61
Lime (CaO)	·27	1·60	·60	·55	·10
Magnesia (MgO) ...	—	—	—	—	—
Soda (Na_2O) ...	14·53	14·90	14·26	13·84	13 89
Total ...	99·75	100·20	100·06	99·79	100 14

MOLECULAR COMPOSITION.

	G.4.B.	G.4.C.	G.4.D.	G.4.E.	G.4.F.
SiO_2 ...	100·0	100·0	100·0	100·0	100·0
Na_2O ...	19·02	19·96	18·99	18·62	18·92
Al_2O_3 ...	8·341	8·849	9·701	10·53	12·07
CaO ...	·3908	2·370	·8835	·818	·1506
MgO ...	—	—	—	—	—
Fe_2O_3 ...	·07114	·1092	·07236	·1044	·07403

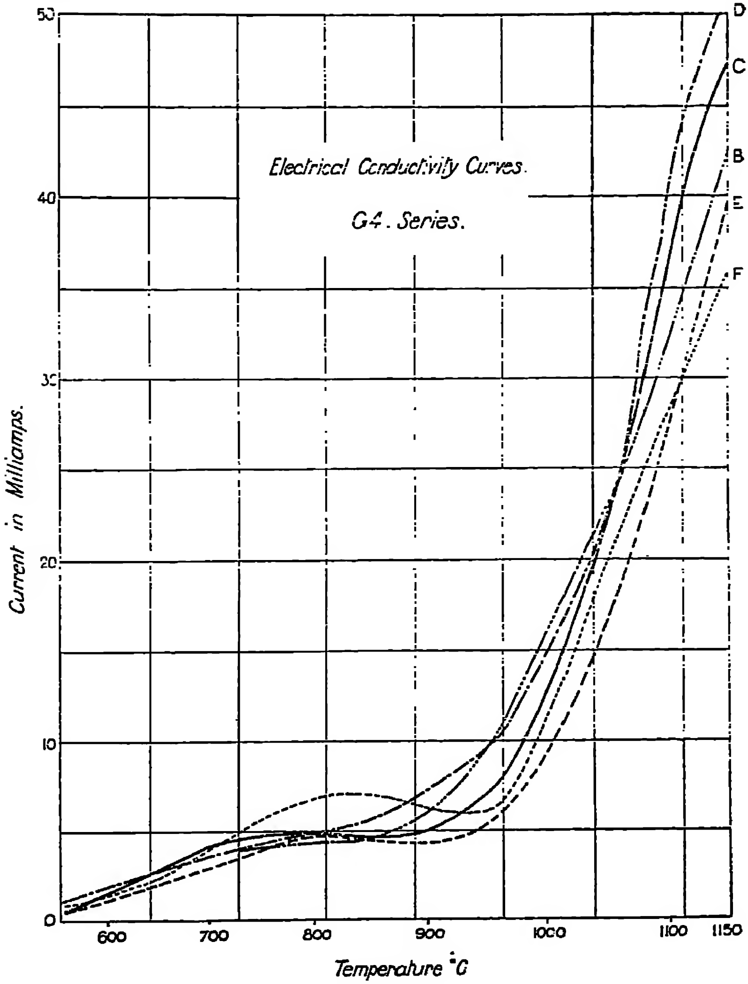


FIG. 6.

Fig. 6 gives the temperature-conductivity curves for these glasses. Glass A was too full of stones from the pot to permit of a test being made. The curves show that increasing Al_2O_3 content produces at the higher temperatures an increase in the conductivity until 10 molecules of Al_2O_3 are present, after which the conductivity diminishes with increasing alumina. It will be noted that below 1050° C. the order of the curves is reversed.

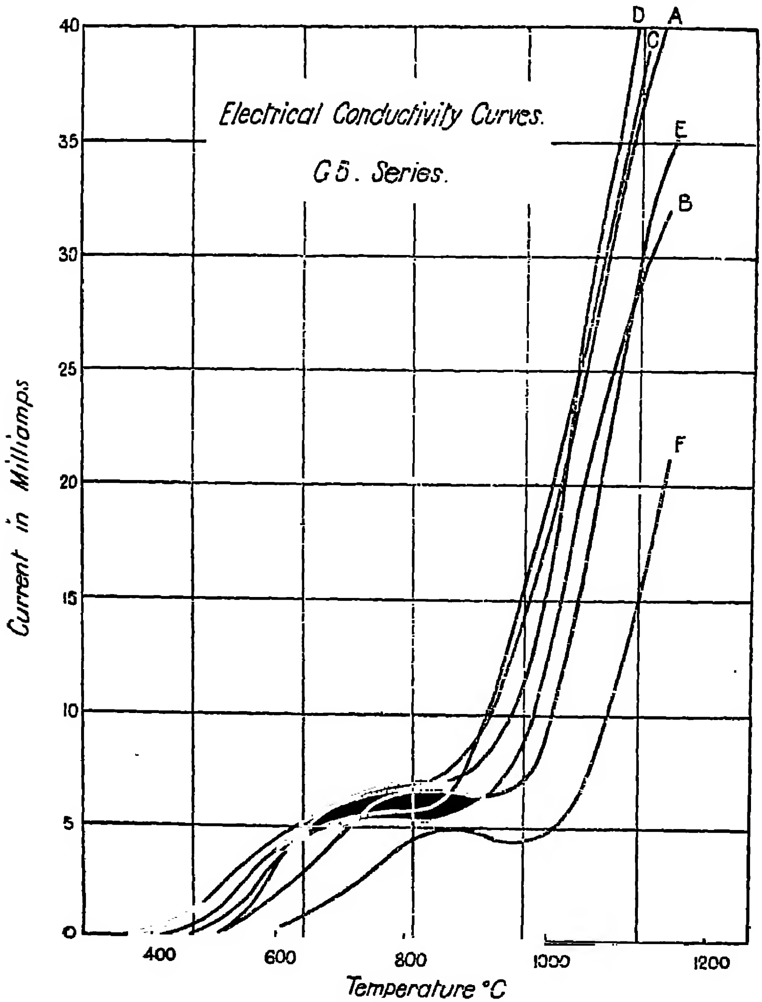


FIG. 7.

SERIES G.5.

Formula 100 SiO_2 x Na_2O y Al_2O_3 (x + y=30).

Calculated molecular composition :—

	A.	B.	C.	D.	E.	F.
SiO_2	100	100	100	100	100	100
Na_2O	29	26	24	22	20	18
... ...	1	4	6	8	10	12

ANALYSES OF GLASSES.

	G.5.A.	G.5.B.	G.5.C.	G.5.D.	G.5.E.	G.5.F.
Silica (SiO_2)	75·70	75·30	73·45	74·10	72·00	72·50
Iron Oxide (Fe_2O_3) ...	·11	·11	·13	·17	·14	·17
Alumina (Al_2O_3) ...	2·29	5·49	8·47	10·58	13·01	15·00
Lime (CaO)	—	—	—	—	Trace	Trace
Magnesia (MgO) ...	·20	·15	·20	Trace	Trace	Trace
Soda (Na_2O)	21·21	18·18	17·81	15·63	14·07	12·24
Total ...	99·51	99·23	100·06	100·48	99·22	99·41

MOLECULAR COMPOSITION.

	G.5.A.	G.5.B.	G.5.C.	G.5.D.	G.5.E.	G.5.F.
SiO_2 ...	100·0	100·0	100·0	100·0	100·0	100·0
Na_2O ...	27·25	23·48	23·58	20·51	19·01	16·43
Al_2O_3...	1·784	4·301	6·803	8·422	10·64	12·21
Fe_2O_3...	·04358	·05516	·06682	·08662	·07341	·08853
MgO ...	·3951	·2980	·4071	Trace	Trace	Trace
CaO ...	—	—	—	—	Trace	Trace

It will be noticed from the analyses that there is a considerable decrease in the Na_2O content between A and B. This probably accounts for the drop in the curve B (fig. 7) at high temperatures. B and C have practically the same Na_2O content and the rise in the conductivity of C at the high temperatures is accounted for by the increase in the Al_2O_3 content. The increased Al_2O_3 content of D causes a further rise, while in E and F with an Al_2O_3 content of more than 10 molecules conductivity decreases. It will be seen from the curves that at a temperature of 900° C. the current diminishes with increasing Al_2O_3 content (the exception, curve B, has already been referred to). It will also be noticed that in the case of A (1·7 molecules Al_2O_3) the conductivity gradually increases with temperature.

In the case of B there is a period between the temperatures 600° C. and 900° C., and in the case of C between 650° C. and 900° C., where the increase of temperature produces no change in the conductivity. In the other cases with higher Al_2O_3 content, there is, in the neighbourhood of 850° an actual diminution of conductivity with increasing temperature, and this diminution increases with increasing Al_2O_3 until in F (12·21 molecules Al_2O_3) there is quite a distinct drop, the curve rising steeply thereafter.

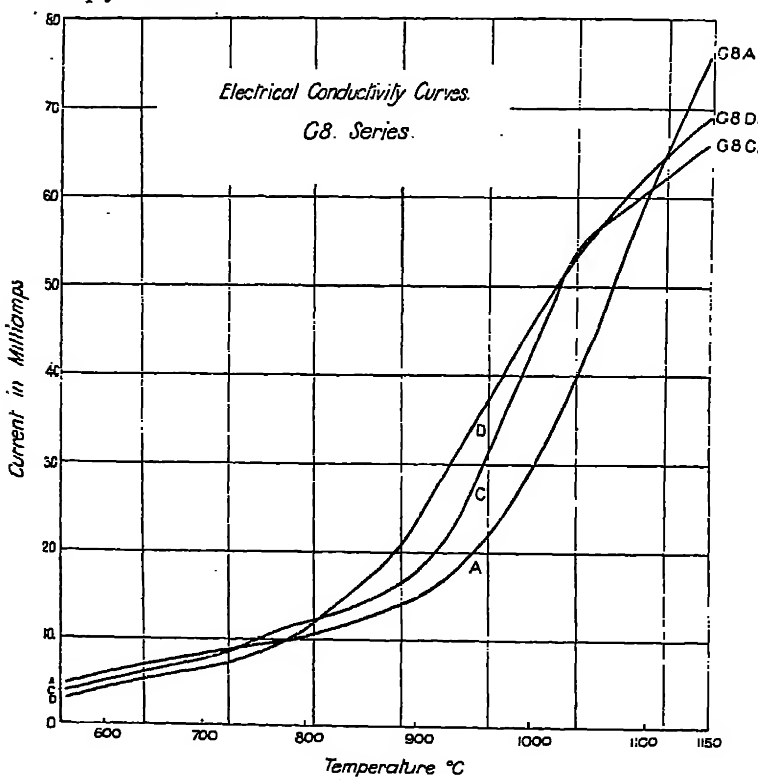


FIG. 8.

Further series of glasses were made in small clay pots in a carbon electric furnace. These glasses were not analysed afterwards, and only the calculated molecular composition is given here.

Series G.8.

Formula 100 SiO_2 40 Na_2O x CaO.

Calculated molecular composition :—

	A.	B.	C.	D.
SiO_2	100	100	100	100
Na_2O	40	40	40	40
CaO	5	10	15	20

Fig. 8 shows the temperature-conductivity curves for three of these glasses. Glass G.8.B. devitrified during the test and consequently the conductivity readings are not comparable. The graphs for these three glasses show that at lower temperatures increasing CaO content is accompanied by diminishing conductivity, but within the range 810° to about 1100° C. increasing the CaO content increases the conductivity, while

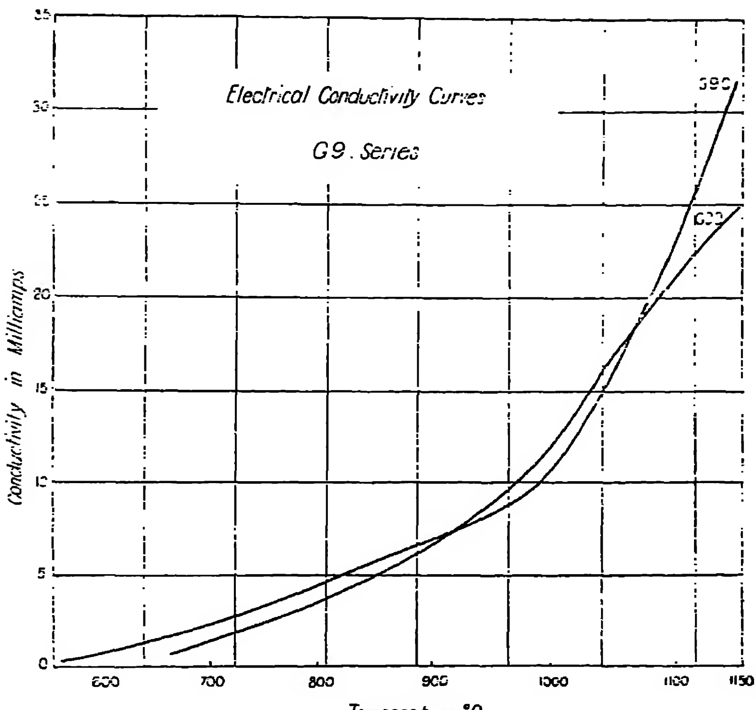


Fig. 9.

above that temperature the glass 8.A. with the lowest CaO content becomes rapidly more conducting than the others.

SERIES G.9.

Formula 100 SiO_2 20 Na_2O x CaO.

Calculated molecular composition :—

	A.	B.	C.	D.
SiO_2	100	100	100	100
Na_2O	20	20	20	20
CaO	10	15	20	25

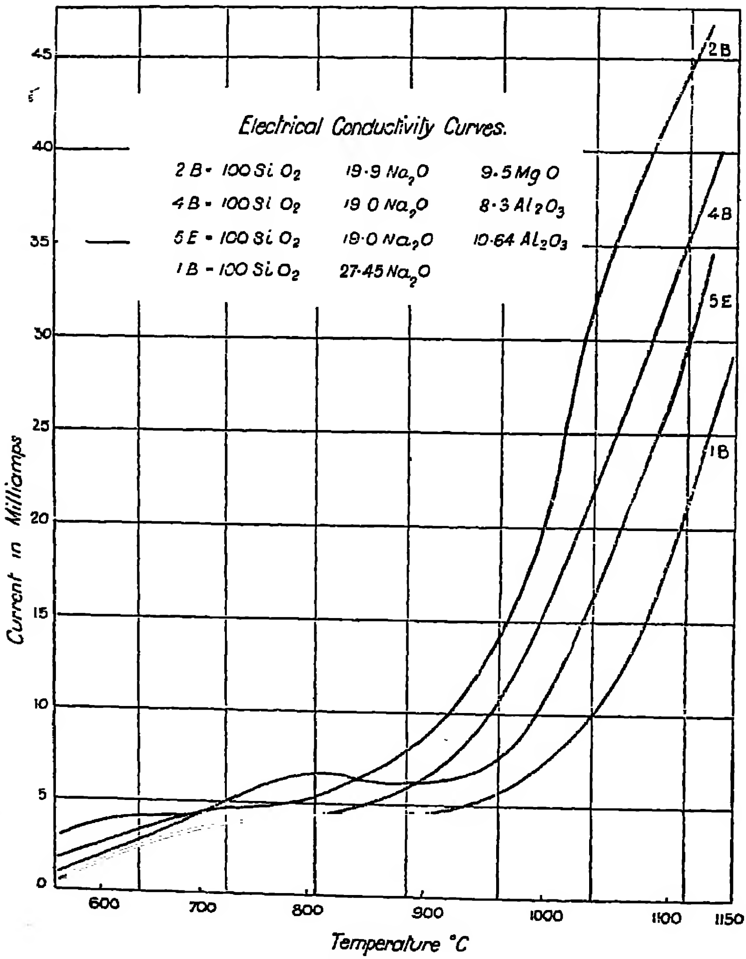


FIG. 10.

Of this series, A devitrified during the conductivity measurements, and B devitrified in the pot. The temperature-conductivity curves for C and D are shown in fig. 9. It will be seen that except within the range 920° to about 1040° C. the glass with the higher CaO content has a lower conductivity than the other. At temperatures below 950° the rate of increase of conductivity with temperature is greater in the case of the higher CaO glass than in the other.

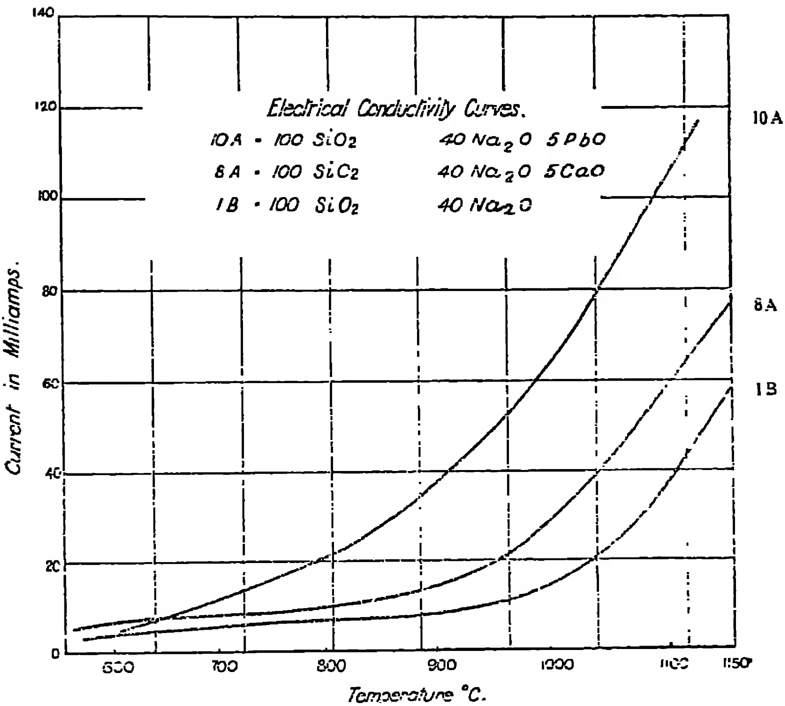


Fig. 11.

For purposes of ready comparison curves for glasses having approximately equal molecular amounts of SiO_2 and Na_2O from different series are plotted on the same scale in fig. 10 which shows that in these glasses MgO has a greater effect in increasing the conductivity of the glass than Al_2O_3.

The curves in fig. 11 show the increased conductivity at high temperatures by the substitution of 5PbO for 5 CaO in a glass of the form 100 SiO_2 40 Na_2O 5 CaO.

Calibration of Conductivity Vessel.

The tubes used for containing the glasses during the conductivity tests have been calibrated, as a result of which the actual conductivity of the glasses at high temperatures may be ascertained, if we assume, as has been indicated, that the conduction is of a purely electrolytic nature. For this purpose a glass tube of the same internal diameter as that of the clay tubes used for the tests was filled with 1/10 n. KCl. Platinum electrodes were sealed into the glass tube at the same distance apart and with the same amount of electrode exposed as in the glass conductivity experiments. The electrodes were platinised in the usual way. The conductivity of the solution was determined in conditions similar to those used for testing the conductivity of the glasses. Taking the value of the conductivity of 1/10 n. KCl at a temperature of 12° C. as ·00979 (ohm.$^{-1}$ cm.$^{-1}$) we get a calibration factor of ·00538 corresponding to a current of 1 ma.

Effect of Change of Frequency.

The current used in making the conductivity tests had a frequency of 500 alternations per minute. Tests were also made with frequencies varying from about 300 to 2,000 per minute, and it was found that for a constant temperature and a constant applied E.M.F., the current through the glass increased with increasing frequency. The frequencies mentioned were the minimum and the maximum obtainable with the motor commutator used.

Works' Scale Experiment.

The graphs show that in general there is a great increase of conductance with increasing temperature. Since the ionisation of the glass varies only little with the temperature, the increased conductance must necessarily be due to the increased speed of the ions at the higher temperatures. That is to say, that the change of conductance due to change of temperature is of the nature of a viscosity effect. As the

viscosity diminishes with increasing temperature, the rate of ionic migration increases in consequence of the diminished resistance which the moving ions experience. A study of the temperature-mobility curves of glasses shows that they are of the same general nature as the temperature-conductivity curves. If there is a close relation between the two then the conductivity may give us a measure of the mobility or the viscosity. This possibility suggested itself in the early stages of the investigation, and accordingly the methods of measurement were kept as simple as possible and of such a nature as might be applied to the measurement of the conductivity of glass flowing from a tank.

Before the relation existing between the mobility and the conductivity of glasses can be definitely determined further data are necessary relating to the relative effects on these properties of alterations in the chemical composition of the glass. In view of the importance of being able to ascertain the viscosity of the glass as it is being taken from the tank, it was considered desirable to make arrangements to test the variations in its conductivity over a considerable period. As it is undesirable to have metal electrodes immersed in the glass flowing from a tank it is necessary to protect the electrodes by a refractory material which will not readily be acted on by the glass. The question of the electrical conductivity of such material as related to that of the glass must then be considered. Experiments were carried out on small test pieces of sillimanite and of pot clay. It was found that when direct current was used polarisation effects were introduced and the current through the test piece was very small even at temperatures of about 1,200° C. and with a voltage of 200. Different electrodes were tried, but all gave somewhat similar results with regard to polarisation. When alternating current was used these polarisation effects were not observed. The alternating current was produced as before, by the use of a motor-driven commutator giving 500 reversals per minute. The method of measuring the current was the same as that used in connection with the glasses, but in order to obtain readings on the recorder the

voltage on the a.c. side was increased to 50, and a standard resistance of 20 ohms had to be used for the small currents at low temperatures. As the temperature and also the conductivity increased this was replaced by one of 10 ohms. and then of 1 ohm. The test piece was moulded into the form of a cylinder 8 mm. in diameter and 13 mm. long, and supported in the small tube furnace on a platinum electrode held in position by means of a fireclay tube. The other electrode, also of platinum, was pressed down on top of the test piece. It was found that in the case of both fireclay and sillimanite the conductivity of a test piece which had been dried but not fired when put into the furnace was much

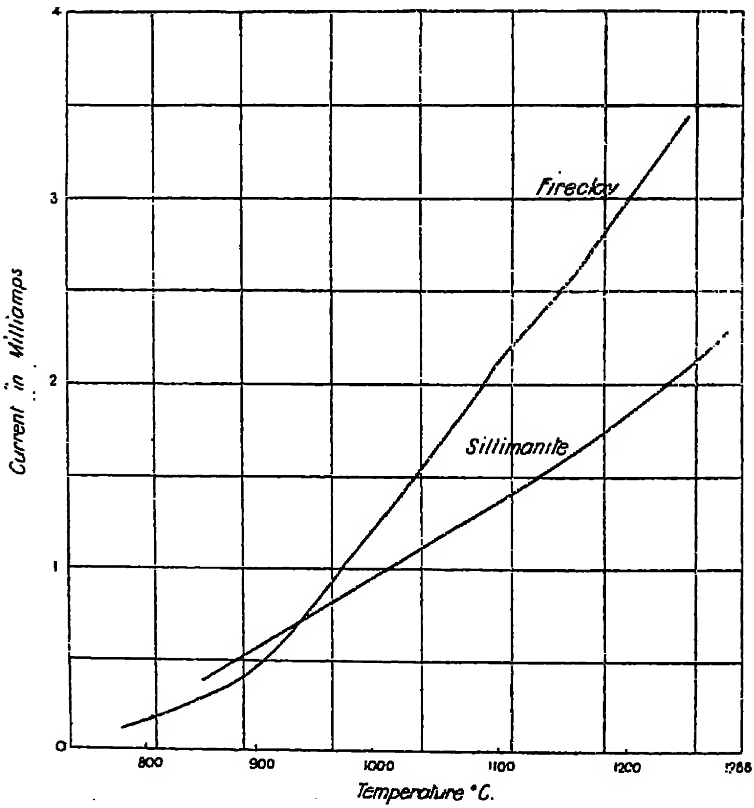


FIG. 12.

lower than after firing. Fig. 12 shows the temperature-conductivity curves for fireclay and sillimanite using test-pieces of the sizes given above. It will be seen that for temperatures above 930° C. the clay has a higher conductivity than the sillimanite.

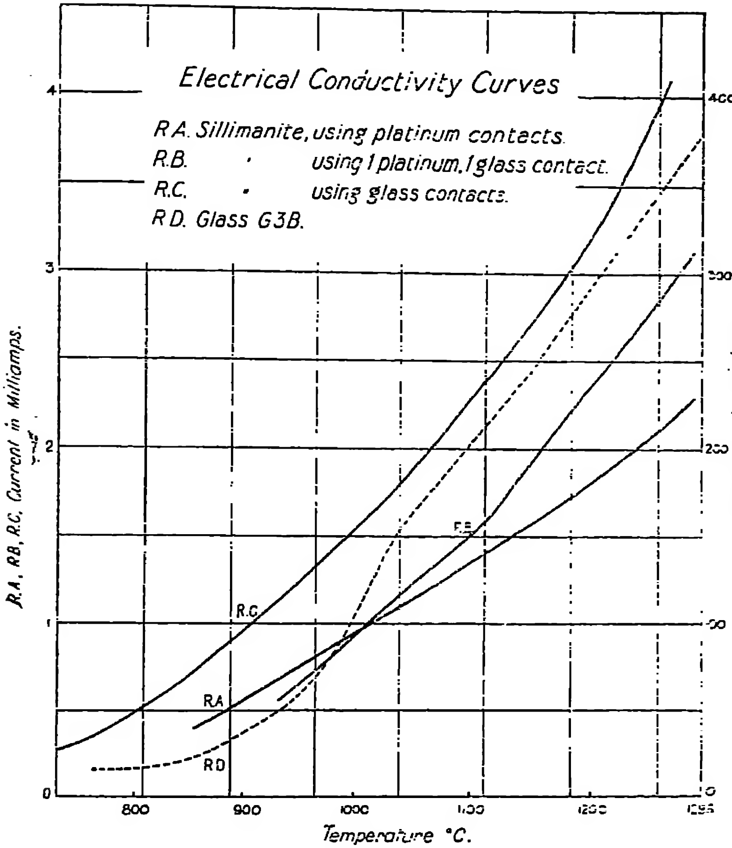


FIG. 13.

When a bead of glass was melted on to one end of the sillimanite test piece and the platinum electrode fused on to it, a considerably increased conductivity was obtained. A bead of glass fused on to both ends of the test piece resulted in a still greater conductivity. Fig. 13 shows the temperature conductivity curves obtained, RA being the curve when

the platinum electrodes are in direct contact with the sillimanite, RB the curve when the sillimanite is coated with glass at one end, and RC the curve when the sillimanite is coated with glass at both ends.

In order to compare these readings with the conductivity of an ordinary glass a cylindrical crucible with an inside diameter just slightly less than the diameter of the clay and sillimanite test pieces was used. The bottom of the crucible was formed by a thermo-couple insulating tube holding in position a platinum electrode of the same shape and size as that used with the test pieces of refractory material. The top electrode was also the same as before. The crucible was filled with glass G.3.B. (SiO_2 73·6; Al_2O_3 4; CaO 4·8; MgO 5·7; Na_2O 11·5) to a depth equal to the length of the refractory cylinders and the top electrode brought down into contact with the surface. The curve (RD) obtained is shown in Fig. 13, the conductivity scale, however, for the glass being 100 times that used for the curves for the sillimanite. It will be seen that at 1,200° C. the conductivity of the glass is about 110 times that of the sillimanite with glass on one side and about 88 times that of sillimanite with glass in contact on both sides. This suggests that if electrodes be introduced into the glass in a part of the tank through which the glass is flowing, the current will pass through the glass rather than through the refractory material of the tank wall; and at the same time it suggests that if the electrodes are protected by refractory materials, the total thickness of this material which has to be traversed by the current before it passes through the glass must be small in relation to the distance between the electrodes.

Through the courtesy of one of our members we were enabled to make the necessary arrangements for conductivity tests on a works' scale. At the works of this firm careful control is exercised over the raw materials used so that variation in the measured conductivity of the glass arising from variation in the raw materials could be accounted for. The channel leading to a Hartford-Fairmont feeder working on the tank was chosen as one of the places

where conductivity measurements might be made conveniently. Although the installation was completed and used for some time, conductivity readings were not taken over a sufficiently long time to enable us definitely to ascertain the relation between variations in the conductivity as recorded and variations in the viscosity as otherwise observed. It may be of interest, however, to give a brief description of the installation. Before the channel leading to the feeder had been used, two electrodes were fixed opposite one another at a position in the channel block about $1\frac{1}{2}''$ below the glass level and sufficiently far back to be clear of the movement of the feeder paddle. At this position the channel block is about $3\frac{1}{2}''$ thick and the width of the channel about 12″. For the insertion of the electrodes, holes were drilled at these points through the channel block, and a sillimanite tube $\frac{5}{8}''$ in diameter and $4\frac{1}{2}''$ long was cemented into each so as to be flush with the block on the inner surface. Sillimanite was used in preference to fireclay as it was considered that the former would be less readily attacked by the molten glass. This sillimanite tube had a bore 3/16″ in diameter, but was closed at the end exposed to the glass in the channel. A bead of glass had been dropped into the tube and melted, and a piece of stout platinum wire inserted. The inner end of this wire was embedded in the bead of glass, thus making contact with the sillimanite. The wire was then securely fixed in the tube by means of alundum cement. The outer end of the platinum wire was welded to a copper cable insulated by means of fireclay insulators. The cable was led along the inside of an iron tube inserted through the brickwork and insulating powder surrounding the channel block. The cable from each electrode was then carried down the side of the channel and underneath the platform to the recording apparatus. The method of measuring the current was the same as that used in the laboratory experiments.

As soon as conditions permit the tests on the works scale will be continued so that continuous readings may be obtained over a prolonged period.

V. The Thermal Endurance of Glass.

Programme of Research,
Ref.: Item 1.

Report from the Department of Metallurgy and Metallurgical Chemistry, the National Physical Laboratory, by Vaughan H. Stott, M.Sc., presented by W. Rosenhain, B.A., D.Sc., F.R.S.

PART I.

Abstract: An analysis is made of the factors influencing the thermal endurance of glass. It is shown that the power of glass to withstand thermal shocks is not a definite property of the particular kind of glass, but depends on the size and shape of the actual object, and on the manner in which the thermal shocks are applied.

It is, however, possible, from a knowlege of certain physical constants, approximately to classify glasses from the point of view of their endurance with respect to a particular type of thermal treatment.

The determination of the thermal endurance of particular articles under normal conditions of use offers considerable difficulties. Any test which may be provisionally adopted as a standard must be regarded as somewhat arbitrary.

In spite of its practical importance, the theory of the thermal endurance of isotropic solids has been somewhat neglected, and in view of the desire of glass manufacturers to have a means of testing the relative values of different glasses considered apart from the actual forms and conditions of use of the manufactured articles, it will be useful to discuss the principles, as far as they are known, of the phenomena involved. It must be emphasised at the outset that these phenomena are exceedingly intricate and in the present state of our knowledge any explanations will necessarily be in some degree defective.

Let us then imagine a glass body free from strain at a uniform temperature θ_0, and let us suppose that the surface is divided into three sections. The first section is in contact with

a body impervious to heat. The second section is maintained at a temperature θ_0. The third section has its temperature suddenly changed to θ and maintained at this temperature. We shall suppose that the glass breaks after a time t. Let ζ represent the maximum deformation which an element of the glass can sustain without rupture. It is to be considered as a function of a uniform dilatation and two shears. It will also, together with the quantities about to be defined, be considered independent of temperature.

Let $D=k/sc$ be the diffusivity (where k is the conductivity, s the density and c the specific heat).

Let the experiments be confined to bodies which are geometrically similar to each other and let l be a length which fixes the size of the body.

Let α be the coefficient of expansion.

It is clear that the body breaks at a time t when the deformation at some point just exceeds ζ. The deformation will be proportional to the coefficient of expansion α and will depend also on the size and shape of the body, on the distribution of temperature, and on two elastic constants which we shall call E_1 and E_2. The distribution of temperature will depend only on $\theta-\theta_0$,on D and on t. (Radiation is not taken into account.) A relation must accordingly exist between ζ, E_1, E_2, D, t, l, α, and $\theta-\theta_0$.

It is convenient to write this relation in the form

$$(\theta-\theta_0)\,\alpha=\phi\,(\zeta, E_1, E_2, D, t, l, \alpha, [\theta-\theta_0]).$$

Let us consider the dimensions of these quantities.

ζ has dimensions		O
E_1 and E_2 have	,,	$ML^{-1}\,T^{-2}$
D has	,,	$L^2\,T^{-1}$
t ,,	,,	T
l ,,	,,	L
α ,,	,,	Θ^{-1}
$\theta-\theta_0$,,	,,	Θ

Hence since $(\theta-\theta_o)\,a$ has zero dimensions the dimensions of the expression on the right-hand side of the equation must also be zero. Let us find what combinations of these quantities exist which have zero dimensions.

Let the dimensions of

$\zeta^j\, E_1^m\, E_2^n\, D^q\, t^r\, l^s\, a^u\, (\theta-\theta_o)^w$ be zero.

Then j is indeterminate.

$$-u + w=0$$
$$m + n=0$$
$$2q + s=0$$
$$-q + r=0$$

Hence we may write

$$(\theta-\theta_o)\,a = \phi\,(\zeta, [\theta-\theta_o]\,a, \sigma, \sqrt{Dt}/\,l).$$

where Poisson's ratio σ is a function of E_1/E_2. The above equation may be rewritten in the form

$$\theta-\theta_o = [1/a]\,f\,(\zeta, \sigma, l^{-1}\,D^{\frac{1}{2}}\,t^{\frac{1}{2}})\,\ldots\ldots\,(1).$$

in which we may substitute $\sqrt{kt/sc}$ for $\sqrt{Dt}$.

Before discussing this relation it is convenient to consider a rather different case.

Let $(\theta_c-\theta_o)$ be the least temperature difference which can cause fracture.

Then we shall have for reasons similar to those above

$$(\theta_c-\theta_o)\,a=\Psi\,(\zeta, E_1, E_2, D, l, a, [\theta_c-\theta_o]\,).$$

where the expression on the right must have dimensions zero. The term t has dropped out because $(\theta_c-\theta_o)$ is the *least* temperature difference which can cause fracture after a time unspecified, and not, as before, the temperature difference which causes fracture after a given time t.

Let the dimensions of

$\zeta^j\, E_1^m\, E_2^n\, D^q\, l^s\, a^u\, (\theta_c-\theta_o)^w$ be zero.

Then j is indeterminate.

$$-u + w=0$$
$$m + n=0$$
$$q=0$$
$$s=0$$

Hence $(\theta_c - \theta_o)\,a = \Psi\,(\zeta, \sigma, [\theta_c - \theta_o]\,a)$.
or $\theta_c - \theta_o = [1/a]\,F\,(\zeta, \sigma) \ldots\ldots. (2)$.

This relation determines whether a given change of temperature does or does not cause rupture. The relation previously obtained, namely,

$$\theta - \theta_o = [1/a]\,f\,(\zeta, \sigma, 1/l\,\sqrt{\tfrac{kt}{sc}}).$$

determines the time which elapses before rupture occurs after a given change of temperature. It is at first sight surprising that the conductivity of the glass does not appear in the expression for $\theta_c - \theta_o$, particularly as it appears in the special case worked out by Winkelmann and Schott. These authors, however, assumed that the time required to break the specimen is the same for any glass, a statement which is only true when the time in question is zero. It is obvious that in this case the conductivity cannot influence the phenomenon, and in other cases the time of breaking is inversely proportional to the diffusivity as shown by equation (1). Another apparently erroneous assumption was also made, the significance of which is too obscure to be discussed. It will be clear from the relations which have been deduced, that if two specimens of glass are similar in all respects except in the value of the diffusivity, the distributions of temperatures and strains will be identical in the two cases for equal values of Dt, including, of course, the particular value of Dt at which the specimen may break. It is very important, however, to bear in mind the conditions under which this result is true. It is supposed that the temperature of a portion of the surface is brought *instantaneously* from the value θ_o to the value θ_c. In practice this can only be done approximately and usually the degree of approximation depends on the conductivity of the glass. Thus, if a good conductor be heated with a flame, the temperature of the heated surface is lower than would be that of a bad conductor similarly treated. The conditions are probably almost exactly fulfilled when the change of temperature is effected by means of a liquid of low vapour pressure. It will also be observed that the size of the specimen should have no influence on the value of $(\theta_c - \theta_o)$. The only experiments available bearing directly on this point

seem to be those by Winkelmann and Schott who found that $(\theta_c \sim \theta_0)$ was 25 per cent. greater for a cube of 1 cm. side than for a cube of 2 cms. side. The difference is considerable but various factors may have influenced the result. In the first place the fracture takes place very soon in the type of experiment under consideration, and the time required completely to immerse the specimen in the quenching liquid may have been comparable with the time of fracture. If this were the case the fracture would be partially due to the unevenness of the temperature distribution on the surface of the specimen. This effect would be greater in the case of the larger body. In the second place it is probable that the strain is greatest at the corners and edges of a cube, and as the corners and edges of the smaller cubes had probably much the same curvatures as those of the larger cubes the conditions of geometrical similarity were not strictly fulfilled. A third factor is due to the fact that the properties of the surface layers of glass differ from those of the interior, and the theory outlined above does not take cognisance of this. In experiments in which the glass is broken by sudden chilling it is, of course, the surface which breaks by being thrown into tension and this factor is probably of considerable importance.

We may say then, that the thermal endurance of a glass is in general proportional to the reciprocal of the coefficient of expansion and to a function of ζ and σ, but that the value of ζ and σ may require modification to allow for the varying properties of the surface. The diffusivity is of minor importance and its effects are not always in the same sense. A low diffusivity has been shown to increase the time required to break the body (see equation (1)). If the change of temperature tending to break the glass is of short duration a low diffusivity may prevent fracture. On the other hand a high value of the diffusivity tends to prevent fracture by reducing the values of the temperature changes at the surface. In the quenching experiments of Winkelmann and Schott the diffusivities of the various glasses should have little or no influence on their breaking temperatures. The available data are sufficient to show that a formula of the form of that derived above, and which does not contain the diffusivity, is at least in as close agreement with the experimental

results as is the formula employed by Winkelmann and Schott. It may be recalled that these authors made use of the expression

$$\theta_c - \theta_o \propto \frac{P\sqrt{D}}{\alpha E}$$

where P is the tenacity and E is Young's modulus. The general formula which we have derived is

$$\theta_c - \theta_o = [1/\alpha]\, F\,(\zeta, \sigma).$$

Assuming approximately that

$$F\,(\zeta, \sigma) \propto (P/E)\,(1-\sigma).$$

we have

$$\theta_c - \theta_o \propto \frac{P\,(1-\sigma)}{E\,\alpha}$$

This formula may be shown to hold strictly in the case of a sphere with the proviso that P will be somewhat smaller than the tenacity measured in the ordinary way, since the material at the surface of the sphere is subject to tensile stress in all directions tangential to the surface instead of in one direction only. Rather similar conditions apply to the case of the cube and we may reasonably assume that

$$\zeta \propto \frac{P}{E}$$

The multiplying factor $1-\sigma$ may not represent exactly the effect of σ in the case of a cube, but since in any case σ varies little from glass to glass it may be admitted as a first approximation.

TABLE I.

No. of glass.	$1-\sigma$	P	$10^7 \cdot 3\alpha$	E	$\theta_c \sim \theta_o$ Obs.	Cal. (Schott)	Cal. (New formula)
21	0.75	6.12	157	5474	148°	148°	148°
34	0.789	8.16	183*	7001	148°	146°	140°
19=5	0.803	6.95	160	7296	(119°)	147°	132°
22=2	0.726	5.76	202	4699	103.5°	124°	122°
25	0.774	8.51	249*	6498	103.5°	116°	113°
24	0.768	6.07	250*	5389	98.5°	90°	96°
23	0.729	7.52	195*	7952	90.5°	101°	98°
31=13	0.747	7.63	261	6296	50.5°	90°	96°
33	0.761	5.32	252*	5512	87°	71°	81°
26	0.776	5.39	248*	5467	88.5°	77°	86°
28	0.769	6.76	283	6626	88.4°	78°	77°
27	0.765	5.56	295*	6780	62.7°	54°	59°
20	0.739	3.53	280	5088	61.9°	42°	51°

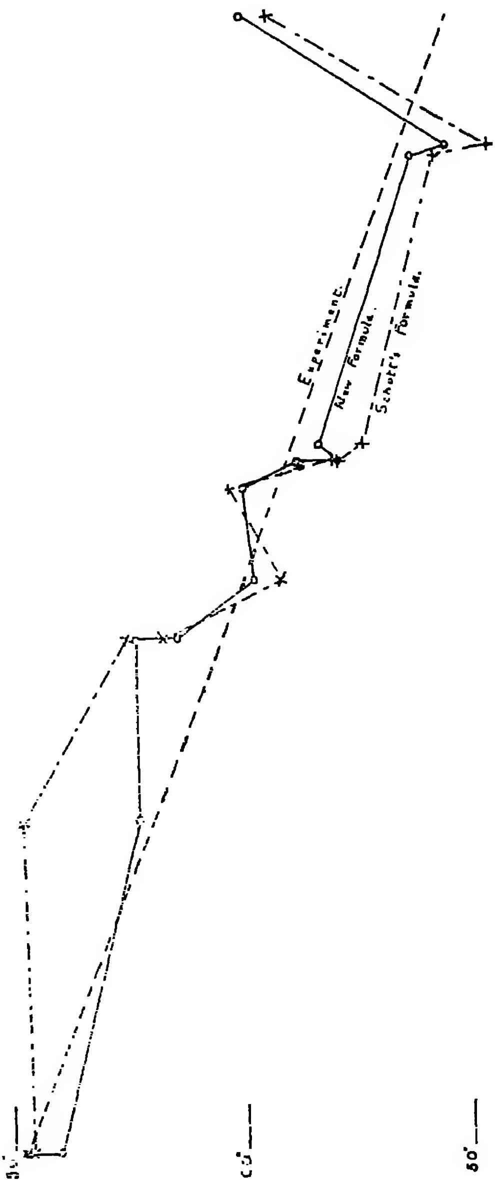
(The values of α marked with an asterisk are calculated from the composition by means of the factors given by Winkelmann and Schott.)

Table I. above gives the values of $\theta_c \frown\!\!\smile \theta_0$ as determined experimentally by Winkelmann and Schott and as calculated from the two formulæ, the constants of proportionality being so adjusted as to obtain identical results for glass number 21. The relations are shown more clearly in the graph. The ordinates represent values of $\theta_c \frown\!\!\smile \theta_0$ and the abscissæ have been arranged so that the experimental results fall on a straight line. For each value of the abscissa which corresponds with an experimental determination there have been plotted the calculated values of $\theta_c \frown\!\!\smile \theta_0$. It will be seen that the agreement with the experimental figures is rendered slightly closer when the calculations are made by means of the new formula than when the Winkelmann and Schott formula is employed. In view of the errors in the data on which all the calculations are founded this difference is quite insignificant. For convenience of reference the compositions of the thirteen glasses are given in Table II.

TABLE II.

No. of glass	SiO_2	B_2O_3	ZnO	PbO	MgO	Al_2O_3	BaO	Na_2O	K_2O	CaO	P_2O_5	Mn_2O_3	As_2O_5
21	32.75	31.0		25.0		7.0		1.0	3.0				0.25
34	70.2	12.0			3.0	4.5		10.3					
19=5	71.0	14.0				5.0		10.0					
22=2		69.1				18.0	4.7	8.0					0.2
25	70.6		12.0					17.0					0.4
24	44.2			47.0				0.5	8.0			0.1	0.2
23	34.5	10.1	7.8			5.0	42.0					0.1	0.5
31=13		3.0				8.0	28.0				59.5		1.5
33	29.3			67.5					3.0				0.2
26	41.0			51.7					7.0			0.1	0.2
28	64.6	2.7	2.0				10.2	5.0	15.0			0.1	0.4
27		3.0			4.0	10.0			12.0		69.5		1.5
20	20.0			80.0									

It is worthy of remark that glass number 31=13, which breaks at a much lower temperature than the calculated value, has a very peculiar composition, containing as it does a very high proportion of barium phosphate, no silica and no alkalies. Divergencies from theory due to the neglect to take into consideration minor factors would naturally be least for glasses of similar compositions since the differences in the minor factors would be relatively small. It is not very surprising then to find that glass number 31=13 does not fall into its proper position.


Experiment.
New Formula.
Schott's Formula.
150°
100°
50°

There is one consideration of great importance with respect to thermal endurance which has been touched upon, but which requires amplification, namely, the differences between the mechanical properties of the surface layers of glass and those of the material well below the surface. In the experiments which have been mentioned as a check on the general rough theory the surfaces were produced by polishing. The general agreement between the experiments and the rough theory which ignores surface effects may be ascribed to the fact that in all the experiments the surfaces were produced by the same process of polishing an annealed piece of glass, and the surface effects of the different glasses in these circumstances are not sufficiently dissimilar greatly to alter the order of the glasses with respect to their thermal endurance. Since the thermal stresses in glass are almost always greatest at the surface there is no doubt that in most cases of thermal endurance the surface properties have a very important influence, and it seems desirable to divide the more fundamental experimental study of thermal endurance into at least two parts, one part dealing with a and the approximate determination of ζ, and another part dealing with the mechanical properties of variously produced glass surfaces. It appears that surfaces polished by fire or otherwise possess a higher resistance to rupture than rougher surfaces. This increased resistance seems at least partially due to an increased plasticity of a polished surface layer which is thus capable of greater deformation without rupture. Rheinberg states, for instance, that an optically worked plate-glass surface may be platinised at a temperature some 10° to 20° C. lower than the unworked surface. This would lead one to suppose that at the same temperature the mobility of the worked surface is about four times that of the unworked surface. The experiments of Auerbach on the hardness of glass show a marked increase in the resistance to rupture of the surface layers compared with that of the interior portions of the glass. When a glass sphere is pressed against the plane surface of a large piece of the same glass the surface of contact is spherical, and has a radius equal to twice that of the original sphere. It would be expected from considerations of dynamical similarity that rupture for a given glass would be determined by the value of d/ρ where d is the diameter of the

depression produced in the originally plane surface and ρ is the radius of the sphere producing the depression. Experiment shows that rupture is determined by the value of d^3/ρ^2, that is, by the value of $(d/\rho)^2d$. It appears from this expression that a given deformation in the surface layers produces a smaller tendency to rupture than a similar deformation of interior layers. It is unfortunately not possible to draw any quantitative conclusion in this connection since the very fact that the surface layers behave differently from those of the interior shows that the principle of dynamical similarity is not strictly applicable to the phenomenon. It should be remarked that the experiments were performed on specimens polished by rubbing. The very interesting experiments of Griffiths have shown that fracture of glass bodies begins normally owing to surface flaws which, under certain conditions, may be largely eliminated with a resultant enormous increase in the breaking resistance of the glass. From the practical point of view it would seem better to endeavour to avoid methods of manufacture which give distinctly bad surfaces than to aim at almost perfect surfaces, for a single flaw may suffice to bring an otherwise perfect surface down to the normal level.

In the foregoing discussion it has always been assumed that the glass considered has been perfectly annealed. It is well known that a certain amount of initial strain may be of great service in improving the thermal endurance of glass ware. Such strain should not be excessive as in "toughened" glass since the increased endurance is produced at the expense of a treacherous instability under ordinary conditions of use. Owing to the large difference between the crushing strength and the tenacity of glass, a specimen in which every surface is in slight compression and the interior in tension is almost always more resistant to thermal or mechanical shock than the same specimen perfectly annealed. The desired increase in resistance may not be obtained if the distribution of strain be too irregular, and it is for this reason that manufacturers usually anneal their wares very thoroughly and obtain regularity of strain by achieving its complete elimination. It should be pointed out that the type of strain which seems most generally desirable is that which

is the most naturally obtained, save for the question of regularity, for compression in the surface of a piece of glass is produced if the surface in question is colder than the interior while the glass cools through the critical range. This is a condition which almost always occurs in practice, and therefore the problem becomes one of accurately controlling the temperature conditions during the fabrication and annealing of the ware. The practical methods to be adopted will vary in each particular case and must, at any rate as regards details, be worked out by the manufacturer to suit his own conditions. Where the thermal endurance of the ware is of great importance most careful attention to the above considerations is essential, and many manufacturers have had experience of good results obtained, often accidentally, as a consequence of " bad annealing." The considerations just outlined lead to a matter of some difficulty, namely, the question of how one can determine whether in a given case a particular distribution of strain is more or less advantageous than some other distribution. It must be emphasised that the problem relates to the particular article and to the peculiarities of its use and not to the glass of which it is made. It is necessary therefore to apply empirical tests carried out under definite conditions which correspond as closely as possible with the conditions of service of the object. The similarity of conditions refers, of course, to the nature of the test and not to its severity.

It is manifest that the testing of finished articles involves considerations quite different from those connected with tests ou the glass itself, and moreover the former must necessarily be of most restricted application. It may, nevertheless, be possible to effect a certain amount of classification and obtain information relative to different general types of articles.

Intimately connected with this classification is a rather different matter which has not in the past received much attention. This is the problem of so designing the shapes of the articles as to produce the maximum resistance possible commensurate with the various limitations necessarily imposed by conditions of use. There is no doubt that the improvements would well repay most careful study of this problem. It is only

necessary to recall the enormous difference between the round and the flat-bottomed flasks to appreciate the possibilities of such work.

In conclusion, it would seem that whilst, from the point of view of thermal endurance, a suitable glass for a specific purpose can be selected from a knowledge of its physical properties, it is more difficult to determine the best methods of making any actual article, or to arrive at a proper method of testing its suitability when made.

It does not appear desirable at the present stage to standardise any specific method of testing for " thermal endurance," in view of the doubt which must exist how far the results of any such test which can be readily applied may correspond with the service behaviour of the product tested.

VI. The Thermal Endurance of Glass.

Report from the Department of Metallurgy and Metallurgical Chemistry, the National Physical Laboratory, by Vaughan H. Stott, M.Sc., and Edith Irvine, B.Sc., presented by W. Rosenhain, B.A., D.Sc., F.R.S.

PART II.

Since Part I. of the present communication was written, some experiments have been made in a similar manner to those of Winkelmann and Schott. The experiments were conducted on centimetre cubes of Chance's optical glass known as B.S.C. 698. The cubes were prepared by grinding and polishing a number of specimens simultaneously. The glass cubes were heated in a vertical tube furnace, and when the temperature was steady they were dropped into a bath of paraffin immediately below the furnace. The temperature of the tube was uniform along its length, and consequently the specimens were only in cold air for about 1/150 second, the first portion of the fall being one of 2-1/2 feet in a region of constant temperature. It was found that a difference of temperature between the furnace and the paraffin of about 250° C. was necessary to cause fracture of the cubes. This result was somewhat surprisingly high since the most resistant glass in the experiments of Winkelmann and Schott could withstand a temperature difference of only 148° C. In their work, however, the specimens were removed from the furnace and plunged into water by hand, and it was thought that the increased speed of immersion in the above experiments might possibly be the cause of the higher resistance. It is readily seen that if the whole surface of a specimen can be chilled instantaneously, and if the glass may be considered as homogeneous, the maximum stress is produced instantaneously at the surface, and the fracture is also produced instantaneously. It is therefore, impossible to immerse the specimen sufficiently quickly to prevent fracture

occurring before the immersion is complete. The fracture in such a case would be due to the local stresses set up by the irregular cooling. On the other hand it is known that the surface of the glass may be somewhat more resistant than the interior, and when the immersion is rapid the difference between the resistance of the surface and that of the interior of the glass may be sufficient to permit of complete immersion before fracture. In this case the greater regularity of cooling conditions as compared with the result of a slower immersion would be expected to lead to a higher resistance. In order to test this idea a series of experiments was performed in which the specimens were caught by means of a piece of muslin so that they were only partially immersed in the paraffin. The difference of temperature required to break the cubes in this way averaged 270° C., the actual values varying from 260° C. to 290° C. The difference of temperature required to produce fracture in the case of complete immersion averaged 250° C. and the actual values varied from 240° C. to 255° C. These results suggest very strongly that in both sets of experiments the fracture takes place as a result of partial immersion. Although this interpretation of the experiments shows that the conditions assumed in the theoretical treatment of the subject given in Part I. are not strictly fulfilled, the effects of the various factors are not very different, and the formula may still be expected to yield comparative results. In particular, since the fracture is apparently almost instantaneous, the conductivity of the glass can be of little importance. Moreover, the fact that the results are influenced by the size of the specimen is readily foreseen if we assume that the fracture takes place before complete immersion. From the point of view of the practical testing of glassware these experiments serve to emphasize the conclusions stated in Part I. of this paper, since in practice rupture must usually be produced by local differences in temperature rather than by the uniform contraction of large surfaces.

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NOTE.

The Council of the Association does not hold itself responsible for the opinions expressed by the contributors of the various articles.

Contents.

Foreword.

THE very able and thorough manner in which Mr. Withey has investigated, analysed and presented in the following pages, the various methods of analysing glass will, I feel sure, be appreciated by every analyst and chemist who has to deal with glass, and though without doubt there will be some who may differ from him in his comments on and acceptations of certain methods, Mr. Withey's conclusions will be confirmed by the majority of practical and experienced glass chemists.

The number of references given, the analyses of work done by leading scientists and analysts, and the conclusions which he has drawn from the published methods used by them, show that Mr. Withey has devoted a vast amount of time and energy as well as painstaking and unprejudiced thought in arriving at his conclusions, and so far as I am able to determine has fairly covered the field of methods to be used in the analysis of the more simple glasses containing silica, alumina, soda, potash, lime, magnesia, manganese, iron, sulphates and chlorides.

I would call particular attention to Mr. Withey's remarks and suggestions upon the fusion method, for in my twenty years' experience of dealing with chemists from various schools, and with varying degrees of practical knowledge, I find that more and greater errors are caused by improperly conducted pre-fusion than in any other stage of the process of analysis, and I therefore suggest that chemists should give this section their particular attention and study.

Mr. Withey's remarks upon the estimation of iron, alumina and manganese, and their separation from each other are also of extreme interest and importance to the analytical chemist, for I think it will be generally conceded that if a piece of glass be broken up and distributed among several chemists, the reports relating to the quantities of each of these elements will vary to a considerable degree; while the summation of the three may be within narrow limits of error, the amounts set down for any one of the elements may vary by 50 % or more. As pointed out by Mr. Withey, errors of this nature are due to choosing the wrong methods of precipitation and separation or improper technique on the part of the operator.

Mr. Withey's "Survey" has been carried out under the direction of the Chemical Analysis Research Sub-Committee, and before putting it into its final form he has had the assistance, criticisms and suggestions of members of that committee which has rendered the work more valuable. It is hoped that Mr. Withey will be able to issue shortly a survey of methods used in analysing boro-silicate, boro-zinc and alumina-silicate glasses, and also methods to be adopted when dealing with the simpler basic glasses containing elements other than those referred to herein. R. L. F.

A Critical Survey
Made for the Glass Research Association of the Methods in Use for the Analysis of the Simpler Glasses

By W. H. Withey, B.A.

I.—GENERAL SURVEY.

IN the present paper it is proposed to examine and criticise the various methods in use for the analysis of glasses of the more common varieties, leaving for another communication the consideration of the less frequently occurring constituents.

The glasses comprised in such a scheme normally contain silica, iron oxide, alumina, manganese oxide, magnesia, soda, and potash, with sulphate, chlorides and sometimes the oxides of arsenic and antimony in small proportions, and will include the soda lime series of glasses. The lead glasses differ only from the above in that they contain lead.

A consideration of the borosilicate glasses containing zinc and other glasses of more complex composition will not be included.

It will be assumed that the ordinary manipulative routine of silicate analysis is known, and attention will therefore only be given to criticisms of methods and recommendations as to the best procedure in order to ensure the most accurate results. Where methods have seemed to possess equal accuracy, the one which in the writer's experience has proved the quicker has been given, but on this point, as on many others, differences of opinion will arise.

It is a matter of some difficulty to recommend schemes for works' control owing to the various requirements of different manufacturers, and the degree of accuracy required.

Suggestions are, however, given under the heads of the various methods for modifications to suit industrial practice where speed, with a certain sacrifice of accuracy, is necessary.

The Limits of Accuracy Possible in Glass Analysis.

Various attempts have been made to determine the degree of accuracy possible in silicate analysis by analyses of synthetic mixtures and in other ways. In some of the results constant errors and accidental errors are added together, while in others only accidental errors are given. The following references may be of service: Dittrich Neues Jahr Min. 2, 69, 1903; Hillebrand. Bull. U.S. Geol. Survey, 305, 26, 1907; Washington " Manual of the Chem. Analysis of Rocks," 24, 1904; see also Mellor Quant. Inorg. Analysis, p. 245, *et seq.*

The whole question is very difficult and complex, and the adoption of *any* standard becomes naturally a matter for personal opinion and experience. It is not unreasonable to suppose, however, that the limits of accuracy for the major constituents are in the order of $\pm$ ·08 calculated on the weight of original material, and that the total for the best analyses should fall within the limits 99·75 – 100·20.

The limits of summation given in the preceding paragraph represent fairly wide limits, and in the present state of analytical chemistry, taking all factors into consideration, it hardly seems possible to restrict more closely this interval. When it is remembered that a glass analysis involves, in the main, a complicated series of double separations on one portion of a sample, with the inevitable risk of losses at each stage the mathematical probability favours a summation less than 100 %, more particularly should this be the case if the more minute traces be ignored. Washburn, Bunting and Footit, for example, have observed that glasses contain from 0·02 – 0·05 % gas, which is invariably ignored.

It will, therefore, be realised that any summation exceeding 100 % should be viewed with slightly more suspicion having regard to the fact that all the precipitates unless carefully prepared and washed are liable to contamination with sodium salts, thus leading to high results. With some glasses containing much alumina or other silicates in which the same holds good the tendency to sums above 100 is particularly noticeable, and may be attributed to the difficulty in completely washing the alumina precipitate.

Methods of Decomposition of the Glass for Analysis.

Only two methods are now in common use:

1. Fusion with sodium carbonate or mixture of sodium carbonate with potassium carbonate.

2. Decomposition with hydrofluoric acid and sulphuric acid, or more rarely ammonium fluoride and sulphuric acid.

Fusion Method.

The general concensus of opinion favours the use of sodium carbonate alone in preference to the mixture of the two carbonates. It has been observed that the fused mass, when sodium is used, is more readily soluble and that sodium salts are more readily washed out from the precipitates than the corresponding potassium salts (*e.g.*, see Dittrich Anleitung zur Gestein analyse, Leipzic, 5, 1905; Reidenbach Uber die quantitative Bestinnug des Magnesiums, etc. Kusal, 69, 1910). Potassium salts also exert a disturbing influence on several determinations (*e.g.*, zinc as phosphate).

There is good evidence for condemning the use of potassium carbonate; it is, therefore not recommended for use in the most accurate analyses.

Decomposition with Hydrofluoric Acid in Conjunction with a Mineral Acid.

In this method the silica is volatilised as silicon fluoride while the bases are left as salts. The method is therefore frequently used in conjunction with the fusion method where time is of importance. It possesses certain advantages but is perhaps more liable to errors than the other method. These chiefly arise from the presence of impurities in the hydrofluoric acid and the difficulty of its complete removal which introduces an error in the alumina determination (Hinrichsen Ber 40, 1497, 1907; Zeit. Anorg. Chem. 58, 83, 1908; Veitch J. Am. Chem. Soc., 22, 246, 1900; Curtman and Dubin. J. Am. Chem. Soc. 34, 1485, 1912).

Owing to the higher boiling point of sulphuric acid, and its ability to destroy organic matter, which is not an infrequent impurity in hydrofluoric acid, it is advisable to use it wherever possible. The presence of sulphates may in certain circumstances introduce an error in the determination of aluminium (Mellor, Quant. Inorg. Analysis, p. 180). This error is not likely to occur if only sufficient sulphuric acid is used to provide a *slight* excess over and above that required to combine with the bases present in the glass. The presence of enough ammonium chloride in the solution used for the estimation of the alumina must not be overlooked since its presence is favourable to inducing complete precipitation. In making use of this method it is always advisable to add the hydrofluoric acid first and to obtain perfect solution, without the application of heat, before adding a sufficient, but not too large excess of sulphuric acid. In this way it is easy to ensure complete decomposition of the glass. A final prolonged heating with the sulphuric acid is essential to remove the last traces of hydrofluoric acid. The use of ammonium fluoride and sulphuric acid possesses no advantage and is not often used.

Hydrofluoric Acid: Pure preparation of: Hamilton Chem. News, 60, 252, 889; Hempel Ber., 18, 1434, 1885. Impurities: Allen Blount, Analyst, 21, 87, 1896.

The Determination of Silica.

This constituent is invariably determined by fusion with an alkaline carbonate followed by the decomposition of the melt with hydrochloric acid. The process depends on the following chemical reaction:

$$Na_2SiO_3+2HCl=2NaCl+H_2SiO_3$$

The silica is separated as silicic acid which on heating loses water and becomes insoluble. It is now realised that the reaction is a reversible one, and that if the dried mass be heated at too high a temperature, recombination of the silica ensues. The old practice, therefore, of prolonged heating at 120° C., or even higher temperature, is now entirely discredited and must be abandoned.

It has been observed that the rate of drying of the residue at 100°—110° C. is relatively rapid in the earlier periods, and that in consequence the amount of silica rendered insoluble in dilute acids soon approximates its maximum, and equilibrium is established between the insoluble silica, soluble silica and alkaline chlorides. If now the insoluble silica be removed and the solution is evaporated again it follows that a similar state of affairs arises, and that if a third evaporation is made only a very small amount of silica escapes estimation. The experiments which have been made leading to this rationale of procedure have been the work of numerous workers amongst whom the following should be mentioned:

Meineke Repert anal Chemie., Vol. 7, 1887, pp. 215, 757.

Cameron Chem. News, Vol. 69, 1894, p. 171.

Gilbert Zeit. Anal. Chemie., Vol. 29, 1890, p. 688.

Hillebrand Bulletin, 422, U.S. Geol. Survey.

The adoption of sulphuric acid in place of hydrochloric acid (Linds Zeit anorg, Chemie,, Vol. 45, 1905, p. 411) although possibly leading to a better dehydration is not to be recommended owing to the errors likely to be introduced

by the presence of sulphuric acid. The following precautions are necessary in the accurate estimation of silica, and epitomise the researches and results of a large body of workers:

1. Fusion with not too large an excess of sodium carbonate. 5-6 times the weight of glass is ample (1).

2. Solution in sufficient water so that on acidification granular silica is formed; since this is more readily washed and is purer than the gelatinous variety.

3. Evaporation to dryness and heating on water bath or in oven not exceeding 110° C. for a comparatively short period (½-1 hr.).* See Gooch and others Chem. News, 110, 1914, p. 202.

4. Solution in dilute hydrochloric acid followed by filtration and washing with cold water.

5. Repeat operations (3 and 4) allowing longer drying periods.

6. In most accurate work repeat again and use platinum vessels for all evaporations.

7. Sufficient blasting of the silica (Gooch) and Hillebrand.†

8. Treatment of residue with hydrofluoric acid and sulphuric acid to determine impurities, followed by blasting and re-weighing of crucible.

9. Addition of silica from alumina precipitate (q.v.).

10. Deduction of any silica from reagents, and correction for loss of weight of crucible.

Two evaporations suffice for any but the most accurate work.

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* Est. of silica. Lenher and Truog, J. Amer. Chem. Soc., 1916, 38, 1050-1063.

† Hillebrand, Chem. News, 1902, 86 pp., 79-89.

Approximate Method for Works Control.

1. Evaporation to dryness and heating for standard time, weighing silica and adding to figure so obtained an empirical correction obtained as the result of an accurate analysis conducted as above. The figure for glasses (66-70%) SiO_2 would be 1-2%.

The following recent papers may usefully be consulted :—

Solubility of Silica in Mineral Acids, Lenher and Merril. J. Am. Chem. Soc., 1917, 39, 2630-2638. Wunder and Suleiman, Ann. Chim. Anal., 1914, 19, 45-49.

The Determination of Iron and Alumina.

In glasses which do not contain any elements which may be precipitated by sulphuretted hydrogen in acid solution, the filtrate, left after removal of the silica following an alkaline fusion, is used for the estimation of iron and alumina. The solution left after treatment with hydrofluoric and sulphuric acids, and containing hydrochloric acid to keep the calcium sulphate dissolved, may also be employed instead. In this case, however, it is not advisable to adopt the basic acetate method of separation.

Two methods only are in common use, viz., separation as basic acetate of iron and alumina, and precipitation by means of ammonium hydroxide. Neither of these two methods is entirely satisfactory. The basic acetate method, although capable of giving good separations from manganese is difficult of application, when the alumina is low in amount, and is, moreover, largely in excess of the iron present. This is the state of affairs with the glasses in question.

Another difficulty arises from the presence of manganese from which alumina and iron are separated by ammonia with great difficulty. (Hillebrand Bull, U.S. Geol. Survey, 422, p. 114). It has been suggested that the manganese iron

and alumina should be precipitated in one group by peroxidising the manganese by means of hydrogen peroxide. (Dittrich Ber., 35, 4072, 1902) or by bromine, in either case adding ammonia as precipitatant.

The precipitation of the iron and alumina is complete in the circumstances, but the separation of manganese is not always so satisfactory; of the two methods the bromine method seems to give more satisfactory results.

Another method is to employ ammonium sulphide and ammonia, but this method is liable to cause an imperfect precipitation of alumina (Fresenius Quant. Analysis, Vol. 2, p. 635), and is also open to objection that some calcium sulphate is liable to be precipitated owing to oxidation of the sulphide to sulphate. To recapitulate, it may be said that none of the above methods is perfect, but that each possesses certain advantages. For convenience it will be assumed here that either the basic acetate or ammonia method will be used and that manganese will be estimated on a separate portion, in analyses of the greatest accuracy, or else precipitated in the filtrates from the basic acetate or ammonia methods.

1. *The Basic Acetate Method.*

The literature relating to this time-honoured process is exceedingly voluminous and the conditions necessary for its successful application are now well known.

To secure the most accurate results, and under the special conditions prevailing with the glasses in question the following precautions must be observed:

1. Sulphates must be absent.
2. Volume of solution should not exceed 200 cc.
3. Final neutralisation with very dilute sodium carbonate solution requires extreme care.*

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* Borck Zeit angew Chem., 1912, 25, 719, recommends the addition of methyl red and then ammonia until colour is changed.

4. The addition of the minimum amount of acetic acid to ensure acidity. (Hillebrand U.S. Geol. Survey Bull., 422.)

5. Dilution of solution at this stage to about 400 cc.

6. Add not too large an amount (2-3 gms.) of sodium acetate to hot solution. (Dibbits Bull. Soc. Chim., 18, 490, 1872. Brearly Chem. News. 79, 193, 1899.)

7. Boiling must be sufficient but not too prolonged.

8. Washing with sodium acetate solution (5%).

9. The solution of precipitate followed by two precipitations with ammonia.

10. Concentration of filtrate and recovery of contained alumina.

Precipitation by Ammonium Hydroxide.

The remarks which were made about the basic acetate separation apply equally to this method. In recent years a considerable number of papers have appeared on the hydrolysis of aluminium salts, and the theory of this method has also received attention. As bearing on this particular problem the following recent papers are of interest:

Blum. Jr. Am. Chem. Soc., 1916, 38, 1282. See also Lundell and Knowles, J. Amer. Chem. Soc., 1922, 45, 676.

Archibald and Habaxian, Trans. Roy. Soc., Canada, 1917, iii., 11, 1-6.

The practice has benefited by these researches with the result that the procedure recommended in the older standard works (Fresenius) has been improved with a considerable saving of time if not accuracy.

The particulars referred to as having been modified are:—

1. Conditions of precipitation.—The long continued boiling is unnecessary and leads to the formation of less pure precipitates and more difficulty in the filtration, and possible loss.

2. The abandonment of pure water for washing.—The modern practice is to use a dilute solution of ammonium nitrate or ammonium chloride as it is found that in this way the precipitate retains its flocculent nature and does not so readily become soluble.

3. The necessity for the complete removal of chlorides is now realised not to be essential although perhaps advisable (Dandt, J., Ind. Eng. Chem., 1915, 7, 847).

The following precautions and conditions should be observed in the estimation of the ferric oxide and alumina and embody the results of the experience of many workers:—

1. Ammonia free from carbonate and other impurities is added slowly in very slight excess to the solution 200-300 cc. at a temperature of 60-70°C (Taylor, Chem. News, 103, 169, 1911), and then boiled for a short period (1-2 mins.).

2. At least 2·5% ammonium chloride must be present to ensure perfect precipitation (Blum. loc. cit.); but more is advisable.

3. Rapid washing with 2-5% ammonium nitrate or 1% ammonium chloride (Dandt and Archibalds loc. cit.).

4. One or more reprecipitations to remove adsorbed salts.*

* The re-solution of the precipitate in nitric acid to avoid the excess of chlorides has been suggested. If this course be adopted, condition 2 must not be ignored.

5. Purification of the ignited precipitate to remove silica (Hillebrand Chem. News, 1902, p. 89, on method), also platinum.

6. Evaporation of filtrate to recover traces of alumina.

7. Regard must be paid to the very hygroscopic nature of the alumina and the necessity for rapid weighings.

Modifications for Approximate Results in Works Control.

One re-precipitation will suffice, and precautions 5 and 6 may be omitted if results are corrected by an empirical factor determined from an accurate analysis. The estimation of silica (5) is however rapidly made and is advisable, having regard to the fact that silica has not been very completely removed in the earlier proceedings.

With practice, working under standard conditions and using papers of similar size containing known weights of alumina, precipitated under similar circumstances, it is comparatively easy to make an estimate by eye with a very surprising degree of accuracy.

The Estimation of Iron Oxide.

The accurate estimation of iron in glasses is a matter of some difficulty owing to the small percentage usually present, and the invariable presence of iron in practically all the materials used in the analysis. Owing to the latter reason, and the difficulty in preventing ferruginous dust accidentally contaminating the solution in the evaporation for silica, it is advisable not to estimate the iron in the precipitate produced on adding ammonia as in the usual course of analysis, but to use a fresh sample of the glass. For the same reason care must be taken to avoid the accidental presence of iron in the preparation of the sample for analysis.

The glass is conveniently decomposed by means of pure hydrofluoric and sulphuric acid, using measured quantities in order that allowance may be made for the iron present in

the reagents. After complete decomposition has been effected and all the hydrofluoric acid has been removed, it is advisable, although not imperative, to dissolve the residue obtained by evaporation in dilute hydrochloric and to precipitate the iron and alumina by means of ammonia.

The precipitate may now be examined for iron in several ways.

1. By volumetric methods.
2. By colorimetric methods.
3. By electrometric volumetric methods.
4. By gravimetric methods.

The most suitable method will depend on the amount present, but for the purer glasses it is practically imperative to use a colorimetric process.

1. *Volumetric Method.*—Suitable for glasses containing percentages of iron above 0·25%, using 2-5 gns. of the glass for analysis. The precipitate is dissolved in sulphuric acid and is then reduced by means of pure zinc, ammonium bisulphite, or sulphuretted hydrogen. If the first be employed the acidity should be about 20 cc. per 100, and care should be taken that the zinc is completely dissolved. If the bisulphite method (Austin and Hurff Chem. News, 46, 287, 1882) is adopted, the acidity should be a good deal less (about 1/3). The complete removal of the sulphur dioxide is tedious and troublesome, and the same applies to sulphuretted hydrogen, but on the other hand both these methods do not introduce any more iron and are reliable in the presence of titania which may conceivably be present. The titration is made with a dilute standard permanganate solution (N/100) carefully standardised against a pure iron solution of the same composition, volume, and acidity. The chief errors arise from incomplete reduction, or removal of the reducing agent and in a lesser degree to too great an acidity of the solution titrated. With amounts of iron given above the method may be regarded as quite satisfactory and accurate.

2. *Colorimetric Methods.*— Perhaps the best known method depends on the fact that on the addition of a solution of a thiocyanate to a ferric salt a red coloration is produced. Unfortunately this reaction is considerably effected by the presence of most other salts, and in the case of pure dilute solutions the colour is not necessarily proportional to the iron, owing to hydrolysis of the ferric thiocyanate. It is, therefore, absolutely imperative to ensure that in every possible respect the standard solution and test solution are identical. To overcome this trouble Tatlock (Jr. Soc. Chem. Ind., 6, 276, 352, 1887) and others have suggested comparing the coloured solution of the ferric salt in ether or other solvents. (*Cf.* Stokes and Cain, Bull. Bur. of Standards, 3, 115, 1907; Gregory, Proc. Chem. Soc., 23, 306, 1907; and others). This procedure increases the delicacy of the test, but is hardly necessary since it is possible to arrange that the standard and test solutions are similar. From the main analysis the total amount of alumina and ferric oxide will be known; hence in preparing the comparison tubes it is possible to add a known volume of a standard aluminium sulphate solution and the same amount of acid used in the solution of the glass for iron estimation. The standard iron solution may be made from a strong solution of ferric sulphate rendered slightly acid and diluted appropriately immediately before use. An alternative method is to dissolve a weighed quantity of pure precipitated ferric oxide in sulphuric acid and to dilute to a convenient concentration. This method avoids the risk of any uncertainty in the composition of the ferric sulphate which is not always of the theoretical value. Whichever method be employed an exact determination of the iron present in the standard should not be omitted. The aluminium sulphate solution may conveniently be made from a pure sample of the chloride which is readily obtained free from iron by treatment of a strong solution with ether in concentrated hydrochloric acid solution (Gooch and Havens, Amer. Jr. Sci., 4, ii., 416). Other reagents have been suggested and used acetylacetonate (Pulsifer, Jr. Amer. Chem. Soc., 26, 967, 1906); Salicylic acid (Smith, Jr. Amer. Chem. Soc., 1, 335, 1879). Also

ammonium sulphide and potassium ferrocyanide. The last two reagents are not very suitable and cannot be recommended. The most suitable dilution to secure the maximum degree of accuracy is largely a personal matter, but in no case should the solution be so concentrated as to cause coagulation of the precipitate. A large excess of the sulphocyanide is essential, and the acidity should be a minimum. Another method depending on colorimetry is based on the yellow colouration due to an acid solution of ferric chloride. The method which was proposed by Huttner (Zeit. Anorg. Chemie., 86, 341-357, 1914) has recently been critically examined by Hostetter, J. Amer. Chem. Soc., Vol. XLI., No. 10, Oct., 1919, with a view to its adoption in glass analysis. The colour is an easy one to match, and to many workers a more satisfactory one than the red produced by sulphocyanide. If due regard be paid to the influence of foreign salts there is no doubt that the method should prove of service in the analysis of the purer glasses.

3. *Electrometric Methods.*—A new class of volumetric method has recently come into vogue in which use is made of the change of electro-potential on the addition of an excess of a reducing agent. A useful review of the literature and method is contained in a paper by Hostetter and Roberts (J. Amer. Chem. Soc., Vol. XLI., No. 9, Sept., 1914). The authors show that it is possible to titrate a ferrous solution without the use of an indicator using 0·01N – ·0005N. bichromate. Such a method is undoubtedly extremely accurate, but entails a good working knowledge of electrical measurements and apparatus. The writer has had no working experience of the method, but on general principles considers it worthy of the attention of chemists.

4. *Gravimetric Methods.*—Except in the case of very impure glasses (*e.g.*, bottles) all such methods are inadmissible.

The Estimation of Manganese Oxide.

The filtrate from the iron and alumina estimation is liable to certain traces of alumina which must be recovered by the

evaporation of the solution. Except, however, in the case when the acetate method of separation has been employed there is little necessity for this precaution except in the most accurate analyses.

The solution, freed from alumina, contains the bulk of the manganese which may be separated by means of bromine or by ammonium sulphide. The former is perhaps easier of application and possesses the advantage of providing a filtrate, which without further modification may be used for the estimation of calcium.

Hydrogen peroxide and other oxidising agents have been suggested in place of bromine, but in the writer's experience possess no advantages.

The essentials required to ensure as perfect a separation as possible are as follows:—

1. The solution must be concentrated (200 cc.).
2. Addition of bromine in slightly acid solution.
3. Followed by excess of sodium acetate (5 gms.) and excess of ammonia.
4. Long digestion at 90° C.
5. Re-precipitation in the presence of ammonium chloride and acetate.
6. Concentration and recovery of traces of manganese from the filtrate.

The precipitate may be ignited and weighed, or if preferred, it may be dissolved and estimated colorimetrically or volumetrically. Two processes are in use and both are accurate.

Bismuthate Process: Reddrop and Ramage J. Chem. Soc., 1895, **67**, 268; Brearley and Ibbotson, Chem. News, 1900, **82**, 269, 1901, **84**, 247, 302, 1902, **85**, 89; Blair, J. Am. Chem. Soc., 1904, **26**, 793; Hillebrand and Blum, J. Ind. and Eng. Chem., 1911, **3**, 374, Little (Analyst 1912, p. 554).

Oxidation by Means of Ammonium Persulphate in the Presence of Silver Nitrate: Walters, Chem. News, 1901, 84, 239; Schmidt (J. Amer. Chem. Soc., 1910, **32**, 965).

In the most accurate analyses a determination of the manganese on a separate sample of the glass is advisable. For this purpose decomposition with hydrofluoric acid and sulphuric acid, and the adoption of the persulphate method may be recommended.

Separation of Manganese by Ammonium Sulphide.

Manganese will under certain conditions when treated with ammonium sulphide separate completely as the green sulphide which is readily filtered and washed. The conditions favourable for this separation have been investigated (Olsen, Clowes, Weidmann, J. Am. Chem. Soc., 26, 1615, 1904). Villiers Compt rendu, 1914, 159, 67). A large excess of ammonium chloride and ammonium sulphide in hot solutions are said to produce the green sulphide. But with the small amounts of manganese which are present in glass and the difficulty in affecting complete separation it is more convenient to employ the bromine method.

The Estimation of Calcium Oxide.

Calcium is almost invariably estimated, after separation, by means of ammonium oxalate. Two methods are in use, in one oxalic acid is added to an acetic acid solution and the boiling solution is treated with slight excess of ammonia. In the second method of procedure precipitation takes place in ammoniacal solution in the presence of solid ammonium oxalate. Both methods give equally good results, but the former is claimed to give a more granular oxalate.

A reprecipitation is essential to remove traces of magnesium and sodium salts.

If the manganese has been separated by means of ammonium sulphide it is necessary to remove this by boiling

with excess of hydrochloric acid, and filtering off the sulphur before proceeding with the estimation of calcium. The following precautions are necessary in order to secure the most accurate results.

1. Solution must contain sufficient ammonium chloride and be concentrated.

2. In the presence of magnesium a large excess of oxalate is required.

3. Sufficient heating to render the oxalate crystalline and consequently less soluble. The solution is allowed to cool and stand.

4. Washing with cold water or dilute ammonia.

5. Recovery of traces of lime from the magnesium pyrophosphate, if present in appreciable amount.

6. Rapid weighing of the ignited precipitate.

The lime is usually weighed as oxide, but it may if desired be weighed as sulphate or carbonate. The last method is the least satisfactory, and of the three, determination as oxide has most to recommend it.

The oxalic acid and ammonium oxalate may contain traces of lime and the lime precipitate may also contain traces of manganese and silica which must be estimated and allowed for in the most accurate analyses.

Modification for Works Control.

The well washed precipitate is treated with sufficient warm dilute sulphuric, and further diluted after decomposition of the calcium oxalate to a degree that will prevent any calcium sulphate separating. The solution is now titrated at 70°C. with a standard solution of permanganate.

The Estimation of Magnesium Oxide.

It is customary after the separation of calcium to evaporate the solution to dryness and expel the ammonium salts, and also remove traces of alumina and silica which have escaped precipitation, or have been derived from the glass utensils during the course of the analysis. For this purpose two methods are available:—

1. *The acidified* solution is evaporated to dryness preferably in a porcelain dish since glass is less resistant and platinum is inadmissible, owing to the presence of nitrates. The dried residue is ignited to remove ammonia salts.

2. The solution is evaporated with a large excess of nitric acid in a well covered vessel.

The second method, if properly carried out, is perhaps the more convenient and requires less attention. There is, however, more risk of loss than in the first method.

There is no real necessity in ordinary analyses to remove the ammonium salts since magnesium is completely precipitated, but more slowly, in the presence of large amounts of ammonium salts. The precipitate will, however, contain any alumina or silica which was previously in solution. The ignited residue obtained by method (1), or the dried mass from method (2), is dissolved in dilute hydrochloric acid and the silica and alumina separated. There is no doubt that the bulk of these precipitates does not represent material from the original glass, but has been derived from the glass and porcelain vessels during the course of analysis. The best course is therefore to ignore these precipitates. An alternative method of somewhat doubtful accuracy is to conduct a blank experiment on the same vessels used, and to accept the difference between the two sets of weights as the material derived from the original glass. The ideal method is, however, to use platinum vessels throughout, but such a course in most laboratories is quite impossible.

Magnesium is estimated as magnesium pyrophosphate after previous separation as magnesium ammonium phosphate. The conditions necessary to obtain accurate results have been very exhaustively examined and must be followed in order to secure the most accurate results.

Various precipitating agents have been suggested and certain advantages have been claimed for each (di sodium phosphate Berzelius, Fresenius, Blum Zeit anal. Chem., 28, 452, 1889; Heintz, 9, 16, 1867), while Mohr Gibbs and others claim that microcosmic salt produces a more perfect precipitation. Both phosphates, however, appear to give similar results. Ammonium phosphate is not to be recommended.

The solution of the ignited residue or the concentrated filtrate is rendered faintly alkaline and precipitated with excess of sodium phosphate or microcosmic salt, followed by addition of more ammonia. Sufficient time must be allowed for complete precipitation.

For the final precipitation the following conditions should be observed.

The slight acid solution is treated with dilute ammonia solution and few drops of sodium phosphate solution until a precipitate commences to form on vigorous stirring. After the lapse of some time about one third more strong ammonia should be added.

Too large an excess of ammonium chloride should be avoided.

The ignition of the precipitate should be made at as low a temperature as possible in a closed crucible and not heated on blast till quite white.

The practice of moistening the grey mass with nitric acid in order to secure more complete combustion causes a distinct loss and should, therefore, not be employed.

The magnesium pyrophosphate is liable to contain traces of manganese, silica, lime, and alumina, which must be estimated and a correction made in the most accurate analyses.

Among the numerous papers on the subject the following are of interest and importance.

Neubauer.—" Ueber die Zuverlassigkeit der Phosphorsaure bestimmung als Magnesium pyrophosphat." Rostock, 1893.
J. Amer. Chem. Soc., 16, 289, 1894.

Reidenbach.—" Ueber die quantitative Bestimmung des Magnesiums als Magnesium pyrophosphat." Kusel, 1910.

Jarvinen.—Zeit Anal. Chem., 1905, 44, 333.

Balaieff.—Zeit anorg. Chem., 1916, 97, 149.

Method for Works Control.

It is possible to titrate the precipitate of magnesium ammonium phosphate by treatment with acid and estimating the amount required to decompose the salt by means of standard alkali. The methods in use have not found such favour owing to the liability to error from the possibility of indefinite composition of the precipitate. The gravimetric method is to be preferred, but the following papers on the volumetric process are of interest and the methods advocated appear to give satisfactory results.

Bruckmiller, J. Am. Chem. Soc., 39, 1917, 610.

Hilbard, J. Ind. and Eng. Chem., 1919, 11, 753.

The Estimation of the Alkalies.

The alkalies are determined on a separate sample of the glass, the bases being finally separated as chlorides which are weighed as such; the potash in the mixture is estimated, its weight calculated as chloride, and subtracted

from the total of mixed chlorides giving the amount of sodium chloride by difference. This procedure, although not entirely satisfactory, is the only one possible owing to there being no reliable method for the direct estimation of sodium.

For the decomposition of the glass two methods are in use :—

1. Decomposition by means of calcium carbonate in the presence of ammonium chloride (Smith's method).

2. Decomposition by hydrofluoric and hydrochloric acids followed by the separation of the other bases in the usual manner when after the removal of the ammonium salts the alkaline chlorides are left. (Berzelius' method.)

The first method is the one more commonly employed owing to its simplicity. It is claimed, however, that the second method gives slightly higher results. In the writer's experience, however, owing to the greater number of manipulations required in the Berzelius process with the inevitable loss which must occur, there is nothing to choose between the two methods.

1. *The Lawrence Smith Method.*

A weighed quantity of the glass (·5-1 gm.) is mixed with its own weight of pure ammonium chloride and 6-8 times its weight of pure calcium carbonate. On heating double decomposition occurs with production of alkaline chlorides which may be dissolved from the mass leaving the other bases behind. The details are well described in the standard works on quantitative analysis or in the author's original paper. (Smith, Amer. J. Science (2), 50, 269, 1871, Chem. News, 23, 222, 234, 1871, also Crooke's " Select Methods of Chemical Analysis.")

A special form of thimble shaped crucible is desirable for the decomposition, but any platinum crucible with a well fitting lid will answer.

The following precautions must be observed in order to secure the most accurate results.

1. The glass must be reduced to the finest possible powder and must be very intimately mixed with the decomposing material.

2. A layer of pure calcium carbonate should be placed above and below the mixture in the crucible.

3. The heating must be gradual in the initial stages until the ammonium chloride is decomposed.

4. The final heating should be conducted in such a manner that the upper portion of the crucible is kept fairly cool. Too high a temperature (above 1,000°C.) is undesirable owing to possible fritting of the mass. One hour at 1,000°C. is sufficient.

*5. In the most accurate analysis it is desirable, after thorough extraction of the mass, to resinter the extracted material, and also to reprecipitate the calcium carbonate to recover traces of alkaline chloride included in the first precipitation by ammonium carbonate.

6. In the case of glasses containing much magnesium the use of an alcoholic solution of ammonium carbonate, in place of an aqueous solution is to be recommended. (Water 180cc., ammonia 800cc., absolute alcohol 900cc., saturate with ammonium carbonate.)

7. The removal of the ammonium salts must be conducted at as low a temperature as possible.

* See Mellor Quant Analysis, p. 225.

8. In glasses containing sulphates care must be taken to convert the alkaline sulphate to chloride by means of barium chloride.

9. A blank analysis must be made on all materials.

The above method, if care is observed in its application, gives good results and compares very favourably as regards accuracy with the methods in use for the determination of the other constituents of glass.

Borzelius' Method: (Pogg. Ann., 1, 169, 1824).

This method is now seldom used and although the results obtained are claimed to be higher than with the Lawrence Smith process, in the writer's experience more consistent results are obtained by the Lawrence Smith process and the risk of losses is undoubtedly considerably less.

The Estimation of Potassium Oxide.

Of the methods in use for the estimation of potassium only two are employed in glass analyses.

1. As potassium platinochloride.

2. As potassium perchlorate.

The former method is the one which has perhaps most adherents, but in recent years owing to the high cost of platinum on the one hand, and an improvement in the manufacture of the materials used in the second process on the other, has made it equally popular with the platinochloride method. As regards accuracy opinion is divided, but both methods may be regarded as satisfactory, and to be equal as regards rapidity of working.

The practice of obtaining the potassium by titrating the mixed chlorides by means of standard silver solution, and from the result calculating the sodium present, is open to so many possible errors that in any but the most approximate

results it should not be used. For works control, however, using pure single alkalies the method may be used. (See however Walker, J. Chem. Soc., Vol. 123, p. 2336.)

The Platinochloride Process.

The fairly dilute solution of the mixed chlorides is mixed with a sufficient, but not too large excess, of hydrochloroplatinic acid and is evaporated to a syrupy consistency. The mass is then treated with 80 % alcohol in which the sodium salt is soluble while the potassium salt is practically insoluble. The following points require attention in order to secure the most accurate results.

1. The hydrochloroplatinic acid should be free from nitrosoplatinic chloride which leads to the production of low results, and on the other hand no hydro chloroplatinous acid should be present, since it leads to the opposite error. (Noyes and Weber, J. Amer. Chem. Soc., 30, 13, 1908.)

2. The solution should be diluted before adding the platinum solution since in this way the crystals are smaller, and less liable to occlude mother liquor.

3. The strength of the alcohol should not exceed 80%, since greater concentration leads to decomposition of the sodium salt. (Morozewicz, Ber. Acad. Sci. Cracovie, 796, 1906. Davis Chem. World, 1, 219, 1912.) In the most accurate results a correction should be made for the slight solubility of the potassium platinochloride. Other washing solutions have been suggested from time to time.

4. The practice of weighing on tared filter papers is not to be recommended.

5. Differences of opinion exist as to the most suitable drying temperature. 100°C. is probably sufficient but 120°-130° is now generally used.

The Perchlorate Method.

The perchlorate method has been critically examined more particularly by W. A. Davis, J. Agric. Sci., 1912, 5, 52, and again more recently by Thin and Cumming, J. Chem. Soc., 1915, p. 361-366. The latter authors point out the danger of impurities, particularly potassium in the perchloric acid, and have worked out the solubilities of potassium perchlorate in the various washing solutions recommended from time to time. As a result of their experiments, they confirm the conclusions of Davis and the method can now be regarded as accurate as the platinochloride method.

It has the advantage that all the metallic perchlorates, with the exception of ammonium, are readily soluble and therefore their presence is not liable to cause the errors possible in the platinum process.

In order to secure the most accurate results attention should be paid to the following details.

1. The perchloric acid must be free from potassium salts (Thin and Cumming loc. cit.). See also R. L. Morris, " The Analyst," 44, 349, and 48, p. 250.

2. Ammonium salts should be absent.

3. The evaporation with perchloric acid must be complete enough to decompose chlorides.

4. The washing solution should consist of a saturated solution of potassium perchlorate in alcohol (98 %) and should have been recently shaken and allowed to settle, to ensure against supersaturation. The greatest care must be taken to ensure that the strength of the alcohol is maintained.

5. The use of alcohol acidified with perchloric acid is not advised.

The Estimation of Lead Oxide.

Glasses which contain lead may be treated as normal soda lime glasses and employing sodium carbonate as flux. It is advisable, however, in such cases to heat at a lower temperature and to keep the upper portion of the crucible, which should be fitted with a good lid, fairly cool as there is a risk of causing slight loss of lead. The practice sometimes recommended of adding potassium nitrate is in the writer's opinion an objectionable one, as it appears to promote the attack on the crucible. Hot water must be employed for washing the silica. By adopting this procedure, the method is as reliable as the alternative method of decomposition by hydrofluoric acid and nitric, or hydrochloric.

Whatever method may subsequently be employed for the estimation of the lead it is necessary to separate the lead as sulphide. The acidity of the solution requires attention, and should be carefully adjusted not to exceed N/10 owing to possible loss of lead on passing sulphuretted hydrogen. The precipitation may be made in the hot or cold, but in the writer's experience precipitation in the cold gives a more readily filtered precipitate.

Several methods are available for the final estimation of the lead. Weighing as lead sulphate is, however, usually employed after solution of the washed sulphide in nitric acid and evaporation to fumes with sulphuric acid. The addition of alcohol to the final solution is unnecessary if care be taken that the acid used is measured and the solution suitably diluted that the acidity is between N/1 and N/2.

Method of Works Control.

The lead may be determined by one of the various volumetric methods, none of which, however, can be regarded as entirely satisfactory.

The following papers give details of the various methods :—

As Lead Molybdate: Sacher Chem. Zeit., 1909, **33**, 1257.

With Potassium Permanganate: Bollembach Zeit., Anal. Chem., 1907, **46**, 582; Chem. Zeit., 1909, **33**, 1142.

Acidimetric Method Employing Hydrogen Sulphide: J.C.S., 1915, p. 989.

The Estimation of the Minor Constituents Occurring in the Commoner Glasses.

The following occur as impurities in the commoner glasses, or are added in small proportions during manufacture. The former include iron oxide, chlorides and sulphuric anhydride, while the latter include the oxides of manganese, arsenic and antimony. Reference has already been made to the estimation of iron and manganese; in the present action, therefore, the other constituents will be included.

Sulphuric Anhydride.

This impurity is invariably estimated as barium sulphate; usually after fusion of the glass with sodium carbonate and washing out the soluble sodium sulphate with water, or a dilute solution of sodium carbonate. As pointed out previously, the use of potassium carbonate is not to be advised and care must be taken during the fusion to avoid possible contamination with sulphur from the coal gas flame. In the most accurate analyses and preferably in all, some method of electric heating is strongly recommended.

The exact determination of sulphur is a matter which has received an enormous amount of attention, and requires great experience and careful attention to detail in order to

secure accurate results. It is impossible in a short memoir to review or criticise the literature relating to the process, but the following epitomises fairly well the details necessary for accuracy. (See very complete and useful bibliography, but more particularly with reference to iron and steel analysis, Pulsifer J. Ind. Eng. Chem., Dec. 1916; see also Allen and Johnston, J. Amer. Chem. Soc., 1910, **32**, 588, 1911, **33**, 82).

The solution derived from the fusion of 1—2 gms. of the glass is carefully acidified with hydrochloric acid, and concentrated to about 100-150 cc., the excess of acid should not be more than 2—3 cc. per 100. To the boiling solution is added very slowly (5 cc. per min.), a moderate excess of a pure 10 per cent. solution of barium chloride, and the solution is allowed to remain on the water bath for some hours and filtered next day. The washed precipitate requires to be ignited in such a manner that there is no risk of possible reduction of the sulphate to sulphide. The chief sources of error arise from the occlusion of foreign salts, including barium chloride, with the precipitate itself. It is doubtful whether any of the suggested after-treatments, *e.g.*, solution of the precipitate in strong sulphuric and pouring into a large volume of water are altogether satisfactory, since with the small precipitates involved the risk of accidental loss may easily exceed the error produced by occluded salts. There is even a risk in the treatment of the residue with hydrofluoric and sulphuric acids to remove traces of sulphur, but fortunately there is not much tendency for silica to contaminate the precipitate. If desired, however, the treatment may be used if care be taken that sufficient sulphuric acid is used. The very accurate estimation of sulphates is, perhaps, one of the processes of analytical chemistry to which most attention has been devoted; and it appears that until some more satisfactory reagent than barium chloride is discovered the result of a sulphate estimation must always be open to a certain amount of criticism.

The Estimation of Chloride.

The chlorides are invariably estimated by means of silver nitrates, either by a gravimetric or a volumetric process. The glass is fused with sodium carbonate and the melt extracted with water to remove soluble chlorides. The solution acidified with dilute nitric acid may be treated by Volhard's volumetric process, or by using the more usual gravimetric process. In the latter case it is always necessary to redissolve the precipitate in ammonia and to filter off any matter not soluble. The solution is again precipitated by adding excess of hydrochloric acid. The chief sources of error arise from the failure to allow sufficient time for the proper coagulation of the silver chloride thus causing loss, which is still further aggravated by using plain water for washing the precipitate in place of very dilute nitric acid. Chlorides may also be estimated when very small in amount by a turbidimetric process. If any such process be employed the greatest care must be exercised to ensure that the standard solution is of the same concentration and composition as the one to be examined. (Richards, Int. Cong. App. Chem., 8, 423, 1913. Guye Jr. Chem. Phys., 10, 145, 1913. Meyer and Stahler Ziet Anorg. Chem., 77, 255, 1913.)

The Estimation of Arsenic and Antimony Oxides.

Arsenic and Antimony are frequently added to glasses during the process of manufacture, and they are therefore present in the finished product. It is unusual to find the two present together.

The elements are invariably estimated on a separate portion to that taken for the determination of the silica owing to the ready volatility of the chlorides on evaporating the hydrochloric acid solution to dryness. The aqueous solution of the sodium carbonate fusion will contain the arsenic and antimony as soluble salts and this solution may be used for their estimation if desired (see Allen and Zies). The addition of a small amount of potassium nitrate to the sodium carbonate used in the fusion is advisable. It is preferable, however,

to use hydrofluoric acid and sulphuric, with a little nitric acid, there being little risk of loss of either metal. Two methods may now be used for the estimation, one is perhaps more convenient when both elements and lead are present, or when a large number of analyses are concerned, while the other is better for single analyses.

Distillation Method.

The solution resulting from the treatment with hydrofluoric and sulphuric acid is distilled with ferrous sulphate and hydrochloric acid in a flask through which passes a current of hydrochloric acid gas. The distillate, if the temperature does not exceed 110°C., contains all the arsenic as arsenious chloride, and on adding a solution of zinc chloride, in order to raise the temperature to 180°C., the antimony may also be obtained in a separate fraction. It is essential that nitric acid be absent, and that some reducing agent be present in order to reduce the arsenic and antimony. The method has been very exhaustively studied and many other reducing agents have been suggested for all of which advantages have been claimed.

Ferrous chloride, ferrous sulphate or ferrous ammonium sulphate are the agents usually employed and are quite satisfactory.

The details of the method were originally given by Fischer (Ber., 13, 1778, 1880), but the method has since been modified by employing a current of hydrochloric acid gas, thus expediting the elimination of the arsenic. (See also Classen Ber., 18, 1110, 1885.)

The details for the subsequent removal of antimony will be found in a paper by Gibbs, Jr. Soc. Chem. Ind., 1901, **184.**

The chief points to be noted in order to secure accurate results are:

1. Freedom of the apparatus, materials and fittings (*e.g.*, rubber) from arsenic and antimony.
2. The absence of oxidising agents and the presence of a sufficiency of a suitable reducing agent.
3. Complete and efficient condensation.

The arsenic may be subsequently estimated by the well-known titration method with iodine due to Mohr. (See Mellor, Quant. Chem. Analy., p. 286, *et seq.*) Antimony may also be determined in the second distillate by a similar method or by Gyory's bromate method (Zeit. Anal. Chem., 32, 415, 1893).

Arsenic, and antimony, may be determined with almost equal accuracy by gravimetric methods in single analyses. If lead be present the sulphate solution remaining after treatment of the glass with hydrofluoric and sulphuric acids, is diluted until the acidity approximates N/2 and the lead sulphate filtered off. In the case of glasses containing antimony such a procedure entails risk of loss of antimony. In accurate analyses, it is therefore desirable to dissolve the lead sulphate in acid ammonium acetate and to reprecipitate the lead as sulphide with sulphuretted hydrogen. This precipitate is treated with sodium sulphide solution to remove possible traces of arsenic and antimony. The main sulphide precipitate of arsenic and antimony, produced on passing sulphuretted hydrogen through the sulphuric solution slightly acidified with hydrochloric acid, is also dissolved in the same sodium sulphide solution. The sulphide solution of arsenic, and antimony, is concentrated and treated with excess of hydrochloric acid and potassium chlorate, to cause oxidation, and boiled under a reflux condenser to remove chlorine. The arsenic may now be estimated as magnesium pyroarsenate. This method, originally suggested by Levol (Ann. Chem. Phys. (3) 17, 501, 1846), has been carefully examined and the sources of error largely eliminated (see, *e.g.*, Hoffmann Beitrage zur Kenntnis der analytischen Chemie des Zinns Antimons und Arsens., Berlin, 1911; Austin Zeit anorg. Chem. 23, 146, 1900).

The practice as at present advocated differs markedly from Levol's procedure and may be epitomised as follows:

The slightly acid solution of the arsenate, and antimony solution containing no ammonium salts, but sufficient tartaric acid to keep antimony in solution, is added slowly to excess of slightly but distinctly ammoniacal magnesia mixture. As soon as precipitation is complete the precipitate is collected and washed on asbestos with the mother liquor, and as small a quantity of pure water rendered faintly alkaline with ammonia. The ignition must not be too intense, and reduction must be guarded against. Owing to the presence of sodium salts it is perhaps advisable to reprecipitate. In the absence of ammonia salts and by employing a magnesia mixture made from chloride (55 gms. $MgCl_2$ $3ONH_4Cl$ and 5cc. NH_4OH, water 1 litre) a correction for the solubility of the precipitate is not recommended. This method cannot be recommended so strongly as the distillation process.

The antimony may be separated by sulphuretted hydrogen from the acidified filtrate and either determined gravimetrically as sulphide, or oxide. With such small quantities, however, a volumetric method is to be preferred.

In the absence of antimony, and for the accurate estimation of traces of arsenic, the Marsh Berzelius process as employed in toxicological work should be employed, usually, however, the arsenic is too large for this method.

Andrews and Fair Zeit fur anorg. Chem., 62, 123, have also suggested a modification of the well-known Bettendorf reaction with stamous chloride for small amounts of arsenic which seems of promise for glass analyses.

Among recent papers on the presence of arsenic in glass one by Allen and Zies J. Amer. Ceramic Soc., Vol. 1, Nov., 1918, is of importance. The authors in addition to determining arsenic in its two degrees of oxidation, have critically examined Levol's method and the iodometric method due to Gooch and Browning (Am. Jour. Sci., 3, 40, 66, 1890).

The separation of the two oxides depends on the fact that arsenious fluoride AsF_3 is volatilised on evaporation with sulphuric acid, while any arsenic in the pentavalent state remains behind. The total arsenic is determined by fusion of the glass with sodium carbonate and a small amount of nitre to guard against loss of arsenic, the silica is subsequently removed by fuming with hydrofluoric and sulphuric acids followed by dilution with water and filtering and the arsenic precipitated as sulphide. The sulphide is then oxidised by means of hydrogen peroxide and either reduced by hydriodic acid and titrated with iodine, or determined gravimetrically as magnesium pyroarsenate as in Levol's method. The paper in addition may be profitably consulted on other points arising in the analysis of glass.

Note on the Estimation of Alumina and Sodium.

In all silicate analyses it is customary to determine both these bases by a different method, but owing to the importance of the accurate determination of these compounds in a series of glasses for research work, such a proceeding is to be deprecated. With the case of sodium, at the present time, perhaps such a course is at least as accurate as any other, but with alumina the same cannot be said. A method of estimation depending on the insolubility of aluminium chloride in other saturated with hydrochloric acid, in which menstruum iron is soluble, has been developed by Havens, Amer. Jr. Sci., 4, v 145, acting on some previous suggestions made by Gooch and Havens, Amer. Jr. Sci., 4 ii, 416. The method might well be adopted in silicate analyses. A modification due to Minnig, Amer. J. Sci., 1915, 197-200, has also been suggested in which acetyl chloride and acetone are used in place of ether.

Methods for Works Control.

For the purpose of controlling the mixing of batches it is sufficient to estimate one or more constituents of the glass, and methods are given in the above paper under the heading of the various bases. Where more complete analyses are

required it is convenient to estimate the silica on one portion, and to take another portion and to decompose it by means of hydrofluoric and sulphuric acid for the estimation of bases. Another time-saving device is to divide the solution derived from either of the methods into two equal portions and to conduct analyses on the two separate fractions.

Attempts have been made to discover more rapid methods for complete analysis, among such schemes one due to Sullivan and Taylor (J. Ind. Eng. Chem., 1914, 6, 897) appears to be fairly satisfactory and worthy of trial.

II.—SUGGESTED SCHEMES OF ANALYSIS.

Preparation of the Sample.

THE sample of glass for analysis should be reduced to a convenient size which may be conveniently done by warming and then moistening with water, another method is to wrap the portion of glass in strong paper and hit with a hammer placing the material on a hard surface for the purpose.

The use of a *good* smooth-surfaced percussion mortar is quite admissible in any but those cases where the iron content is under dispute, and if care be taken not to reduce the material to too fine a consistency and to free the powdered mass from possible fragments of iron by the application of a powerful electro magnet. The dangers of iron contamination with a good hardened percussion mortar have not proved to be serious in practice, but perhaps on general consideration its use should not be recommended.

The glass is now reduced in size by grinding in an agate mortar. The degree of fineness required for analysis for silica and the main constituents need not be excessive, and moreover too fine grinding is fraught with a certain degree of danger owing to the wear on the agate pestle and mortar which will increase the silica content. (See Hempel, Zeit. Angew. Chemie. 14.843. 1901. James, Chem. Eng. 14.380. 1911.)

Powder which will pass through a standard sieve of 120 meshes to the inch will be found to be very readily decomposed on fusion with sodium carbonate.

The very finest grinding is of course imperative in the case of the alkali determination by the Smith method, and in this case the glass must be of such a consistency that when rubbed under the ball of the finger on paper no grittiness is felt.

Since all fine powders are hygroscopic it is necessary to dry the powder at 100° C. before weighing out the sample for analysis otherwise a very serious error may be introduced.

Scheme of Analysis where the Greatest Accuracy is Required.

The chief sources of error in the various methods of analysis have been fairly well indicated in the preceding pages, but the details of the actual manipulation have not been given. In recommending any method of routine a certain difficulty arises. A line of procedure which may work satisfactorily with one analyst may not prove so expeditious as another, intrinsically as good, in the hands of one equally experienced.

The writer, therefore, in advocating a line of procedure which, in his hands has proved reliable, realises the above limitations, but at the same time considers the details of the routine may prove useful to those commencing the analysis of silicates.

Fusion.

1 gm. of the powdered dried glass is mixed with not less than 4 and not more than 6 gms. of pure analysed anhydrous sodium carbonate, in a *smooth* platinum crucible of about 30 gms. in weight. It is advisable to place a thin layer of the carbonate at the bottom of the crucible and another on the surface of the shaken-down mixture.

The crucible is now heated to very dull redness for, say, 10 minutes, in order to effect the bulk of the decomposition of the glass without melting the mass, since in this way there is less risk of loss by the spattering of the molten mass.

The temperature is now raised sufficiently high to melt the mass and maintained until a clear fusion is obtained. The adoption of too high a temperature over a long period results in the production of a less soluble cake. With lead glasses it is advisable to keep the temperature as low as possible and to place the crucible in a hole in asbestos board in order to

keep the upper portion cool to avoid possible loss of lead oxide should the temperature become too high. Ten minutes' fusion at the higher temperature is usually adequate.

The crucible containing the melt is now placed to cool in water, and when quite cold the crucible is about half-filled with water and heated rapidly over a small flame. This procedure followed by cooling and again heating results in some liquid penetrating below the cake causing it to become detached as a button, which is now placed in a porcelain or platinum dish with about 100-150 cc. of water. The dish is now covered and heated on the water bath for some time in order to dissolve as much of the cake as possible. Hydrochloric acid is cautiously introduced by means of a pipette placed under the cover glass and the solution heated under the cover until all the gas has been liberated. The crucible is next cleaned with acid and the contents added to the dish. The cover is rinsed and removed, and the solution allowed to evaporate until crystals of sodium chloride make their appearance. At this stage the whole is vigorously stirred until the mass is practically dry and of a sandy consistency. The adoption of a fairly large volume of water for the solution of the cake conduces to such a result and largely prevents the production of gelatinous silica which takes a long time to dry and is moreover less pure than the sandy variety.

The dish is now covered and placed in an air oven for about 30 minutes at 105-110° C. until the residue smells only faintly of hydrochloric. On cooling the mass is just moistened with hydrochloric, then by sufficient water to dissolve the mass. This is followed by digestion on the water bath for about 10 minutes and the liquid filtered. Two successive additions of water feebly acidified and allowed to digest with the bulk of the silica are followed by the transference of the silica to the paper and washing until chlorides are removed. The whole procedure is again repeated with the solution, and in the most accurate analyses even once more, but in this case the use of platinum vessels is desirable as the third evaporation would probably result in as much

silica being removed from a porcelain dish as would otherwise be retained in solution. The porcelain dish should be allowed to dry, as in this way it is easy to see whether all the silica has been transferred, any silica remaining appearing as slight rough patches on the smooth glaze.

The silica and the various papers are placed in a weighed platinum crucible *very carefully,* ignited with the lid on; when the paper is charred the lid is removed, and after the mass is white the crucible is heated at the temperature of a powerful blow pipe flame and weighed until constant. Two weighings are essential owing to the hygroscopic nature of the ignited silica.

The small amount of impurity in the mass is determined by moistening with water followed by sufficient pure hydrofluoric acid to dissolve it and one drop of sulphuric acid, evaporating to dryness and igniting and weighing. The residue minus the residue from the reagents representing the impurity in the silica. Some minor corrections for the silica have to be made, and allusions will be made to them in the sequel.

Al_2O_3
Fe_2O_3

Iron Oxide and Alumina in the Absence of Metals Precipitated by Sulphuretted Hydrogen.

The solution is concentrated by evaporation to 200 cc. about 5 gms. ammonium chloride added in the form of a solution followed by heating to 70° C., and the addition of ammonia in very slight excess. The solution is boiled for a short period (1-2 minutes), and the solution rapidly filtered and washed with hot feebly alkaline 2 % ammonium nitrate coloured blue with litmus. This results in the precipitate becoming coloured and enables one to see at once when all the precipitate has been removed from the paper which may be done quite readily after washing 5 or 6 times by opening it and washing off with water. The filter paper is treated with hot diluted hydrochloric acid and thoroughly washed. A second precipitation is made under the same conditions as before and the precipitate is washed until all chlorides are removed.

The precipitate may be ignited wet in the platinum crucible containing the residue from the silica since this residue, if the weight does not exceed 1-2 milligrams, may be regarded with practically no risk of error as consisting of ferric oxide and alumina. The precipitate must be ignited at the highest temperature cooled in a good desiccator and weighed twice at least, the result of the first weighing enabling the second to be made rapidly, which is very essential owing to the very hygroscopic nature of the precipitate.

The mother liquor, rendered slightly acid, is concentrated again to about 200 cc. made slightly alkaline, and any small precipitate of alumina added to the main portion.

In the most accurate analyses it is necessary to correct the weight of the alumina precipitate since it may contain traces of silica. For this purpose a weighed quantity, 8-10 times, of sodium bisulphate, the impurities of which are known, is added to the precipitate which has been disintegrated in the crucible by rubbing with a glass rod and a few drops of water.

The bisulphate is cautiously heated until finally the alumina is dissolved. The molten mass is dissolved in dilute sulphuric acid, any insoluble particles being filtered off and rendered soluble by a fresh amount of bisulphate and fusion.

The silica is removed by allowing the solution to evaporate until sulphuric acid fumes are evolved, the solution is diluted and filtered, and the silica thus found is added to the amount originally obtained.

It will sometimes be found, especially with new platinum ware, that a loss of weight is noticed as a result of the prolonged blasting of the silica; in such cases it may be advisable to dissolve the small residue from the silica in bisulphate, clean and re-weigh the crucible, making the requisite correction for the silica determination. Such correction, however, is of doubtful value since the attack by

bisulphate is by no means negligible. The loss of weight of platinum ware on heating cannot be ignored, and the most accurate way of making corrections, for it must be left to the discretion of the analyst, it being sufficient at this point to indicate the possibility of the error.

Fe_2O_3 The Estimation of Iron Oxide.

With the less pure varieties of glass containing upwards of 0·3 % ferric oxide it is sufficient to reduce the above solution of the oxides in a suitable manner (*e.g.* by zinc) and to titrate with $\frac{N}{100}$ $KMnO_4$, observing the precautions noted on p. 16.

If desired the iron may also be determined in a separate portion by a colorimetric method, using a solution of sulphocyanide. The decomposition of the glass is made with hydrofluoric and sulphuric acids, followed by separation of the alumina and iron oxide with ammonia, dissolving the precipitate in hydrochloric acid, and employing a standard solution of ferric iron prepared from an analysed sample of a ferric salt and made up to a convenient strength immediately before use. A convenient strength is ·0001 gms. per cc.

It will be necessary to use an aliquot part of the alumina and iron solution and to arrange that the acidity and all other conditions are the same for both standard and unknown solutions before adding a solution of potassium sulphocyanide. If it is decided to use the bisulphate solution of the mixed oxides the blank solution should also contain a similar proportion of bisulphate, and in the case of rich alumina glasses some alumina as well.

The exact details as regards dilution are matters for individual trial, suffice it to say that the concentration should preferably be dilute enough to prevent the formation of a precipitate and not too dilute in order to avoid errors of multiplication.

Note.

If the separate estimation of manganese be employed it is convenient to precipitate the manganese as oxide with the iron oxide and alumina by means of bromine and ammonia. The objection, however, to this procedure is that owing to the somewhat concentrated ammonia required there is a risk of loss of alumina, and this involves loss of time, so that very little is gained by the joint precipitation of the manganese and alumina.

The Estimation of Manganese Oxide. MnO.

The difficulties attending the separation of iron oxide and alumina from manganese have been referred to on p. 11 *et seq.*, and in the most accurate analyses it is perhaps more convenient to estimate this constituent on a separate sample. Whether this course be adopted or not it will be still necessary to separate the manganese from the filtrate after the separation of alumina.

The solution is therefore treated as indicated on p. 19, the manganese being estimated as oxide on ignition or by a volumetric process. Of the latter the bismuthate method may be recommended. The precipitate is dissolved in a few drops of sulphur dioxide solution and 20 or 30 cc. of nitric acid 1·1 s.g., and then boiled. On cooling sufficient sodium bismuthate is added to complete the oxidation and to provide an excess. The solution is filtered through asbestos pulp, and washed with 10 % nitric acid. A weak standard solution of ferrous ammonium sulphate is added, the excess being determined by the addition of a standard solution of potassium permanganate ($N/_{20}$) 1 cc. = ·00071 MnO.

In the most accurate analyses it is advisable to estimate manganese on a separate portion, owing to the loss of manganese which occurs in the usual method of analysis arising from the difficulty of making complete separations.

For the estimation the following procedure may be recommended. One to two gms. of the finely-ground glass are mixed with a little water in a platinum dish and sufficient hydrofluoric acid added to complete the decomposition (25-30 cc. per gm.). After warming slightly for some time a calculated slight excess of dilute sulphuric acid is added, and the solution is evaporated until the whole of the sulphuric acid has volatilised. The residue is dissolved in 1·2 nitric acid, and to the quite cold solution sodium bismuthate is added. The manganese is thereby oxidised to permanganic acid and determined as given above.

In the case of high lead glasses it may be advisable to filter the solution after adding the nitric acid and before adding sodium bismuthate, but should this course be adopted it is necessary to filter through asbestos to avoid the introduction of organic matter. The hydrofluoric acid sometimes contains organic matter, and to prevent its possible interference it is advisable to add only a few grains of sodium bismuthate in the first instance, and then boil the solution in order to decompose it. A few drops of ferrous sulphate are now added to decompose the permanganate and to dissolve any precipitated manganese oxide, and on again boiling and cooling the main bulk of sodium bismuthate is added, and the process proceeded with as outlined above. The method may also be employed to estimate the manganese obtained on igniting the precipitated oxide, or in any precipitate which is deemed to contain manganese, it being merely necessary to dissolve it in a sufficient excess of 1·2 nitric acid before oxidising with sodium bismuthate.

CaO. The Estimation of Calcium Oxide.

The solution remaining after the separation of the manganese is concentrated to 200-300 cc., and to the boiling solution which has been rendered slightly alkaline 2-3 gms. of solid ammonium oxalate are added. The solution is digested for some time in order to render the precipitate

more granular, and after cooling for two to three hours is filtered and washed with cold water. The use of cold water is advocated owing to the solubility of calcium oxalate which is by no means negligible at higher temperatures. The solution is filtered and the precipitate dissolved in hydrochloric acid. The second precipitation is made as before, but with only the addition of a few crystals of ammonium oxalate before the addition of ammonia. The precipitate is ignited and weighed either as carbonate oxide or sulphate, the relative advantages of which have been discussed in the previous part of the pamphlet.

The Estimation of Magnesium Oxide. MgO.

As was pointed out in the previous portion of the pamphlet there is no real necessity to remove ammonium salts previous to the precipitation of magnesia as phosphate, but as was noted in such cases, there is a possibility of contamination of the precipitate. The author, therefore, recommends that the solution left after the separation of the calcium be treated with 50-70 cc. of concentrated nitric acid and heated in a covered beaker until the evolution of gas has ceased. The liquid is now evaporated to dryness and the residue taken up in dilute hydrochloric acid, any traces of silica removed by filtration and alumina possibly manganese, or even zinc from the glass beakers, removed by treatment with ammonia and ammonium sulphide before the addition of sodium phosphate to that containing the magnesia, which should be slightly alkaline. Two precipitations are essential, and the conditions to be observed are clearly indicated on p. 23.

In very accurate analyses it is perhaps necessary to examine the ignited phosphate for possible impurities as the amount being small any foreign matter would produce a large relative error.

The magnesium pyrophosphate precipitate should be completely soluble in dilute nitric acid, thus showing freedom from silica. The solution should also not give a colouration

on the addition of sodium bismuthate, if, however, a pink colouration is produced the manganese present may be estimated as indicated under the heading, " The Estimation of Manganese," and any thus found deducted as $Mn_2P_2O_7$.

Calcium is very rarely present, its presence, however, is indicated by solution in dilute sulphuric acid, filtering if necessary, and adding 10 times the volume of absolute alcohol, when any calcium sulphate remains insoluble and may be filtered off, dissolved in acid and estimated as oxalate.

K_2O
Na_2O

The Estimation of Alkalies.

The Lawrence Smith method is perhaps the most convenient one to use.

For the purpose ·5-1 gm. of the glass, which must be reduced to an impalpable powder, is mixed with its own weight of ammonium chloride and 3-6 gms. of pure calcium carbonate. The mixture is placed in one of the special crucibles employed for the purpose, or in default one with a closely-fitting lid will suffice. Before introducing the mixture some calcium carbonate should be placed at the bottom of the crucible, and after adding the powder another layer placed at the top, the whole being shaken down by tapping the bottom of the crucible. The crucible must be so heated that the top is kept cool and in the initial stages a very small flame is used until the ammonium salt is decomposed. This is followed by heating to bright redness for one hour.

After cooling, the mass which should not be badly fritted, is covered with water and allowed to stand until the lime slakes, when it will be found that the whole is reduced to a finely divided mass. If, however, this is not the case it is desirable to transfer the residue to an agate mortar with a small amount of water and grind until no large particles are felt. The chlorides are extracted by boiling with three small portions of water in porcelain or platinum, and finally the mass is transferred to a filter paper and washed. It is impossible to get the washings perfectly free from chloride

probably owing to the presence of basic chlorides in the mass; it is, therefore, somewhat difficult to decide when all the alkaline chlorides have been removed. A volume of 250 to 500 cc. used in small portions may be regarded as ample for the purpose, but in high alkali glasses, especially in the case of potash being present, a refritting of the mass is to be recommended in analyses of the highest accuracy.

The solution thus obtained is rendered slightly alkaline with ammonia and to the warm, but not hot, liquid a solution of ammonium carbonate is added in slight excess. The liquid is heated on the water bath until the calcium carbonate has become granular and is then filtered. In very accurate analyses this precipitate should also be dissolved and reprecipitated for the reasons given above.

The solution is evaporated to dryness in platinum and the ammonia salts removed by very cautious ignition since too high a temperature by causing a rapid evolution of fumes may easily lead to serious loss by mechanical means. The residue is taken up in water (5—10 cc.) a little ammonia added followed by a few drops of ammonium oxalate solution and the whole boiled. This solution should be allowed to stand for several hours in the cold and then filtered and evaporated, the ammonia salts being driven off as before. The mixed chlorides left in the weighed dish is heated to about 400-500° C. until constant in weight. The residue is hygroscopic, and due precautions must be taken to guard against absorption of moisture in weighing.

With glasses which contain sulphates a slight error would be introduced in this process unless a slight modification were made and the sulphates converted into chlorides by means of barium chloride.

The Estimation of Potassium Oxide. K_2O.

The mixed chlorides obtained in the preceding process are used for the determination of potassium, the sodium in default of a really satisfactory process being determined by difference.

Two methods for the estimation of potassium are in use, and each has their advocates.

The platinochloride method is preferred by the author, and the procedure employed is as follows.

The mixed chlorides are dissolved in about 15 cc. water, and any insoluble matter filtered off and weighed an allowance being made. To the solution is added a slight excess of a solution of pure hydrochloro platinic acid of such strength that 1 cc. = ·1 gm platinum. Since in this way it is easy to calculate the volume required, it being merely necessary to multiply the weight of chloride by 17 to give the number of cc. required and to add an excess of, say, ·2 cc.

The solution is evaporated to a syrupy consistency on a gently boiling water bath in a place free from ammonia fumes. On cooling 10-15 cc. of 80 % alcohol is added and the whole stirred with a glass rod and allowed to stand for half an hour. The liquid is filtered through a weighed Gooch crucible packed with asbestos, and the mass digested with two subsequent amounts of 5 cc. of 80 % alcohol, the precipitate finally being washed until the washings are not coloured. The precipitate is now dried to constant weight. If the precipitate is made in dilute solution as suggested and the mass well broken up, small crystals alone are produced and a temperature of 110° C. is ample. A correction may be made for the solubility of the salt in 80 % alcohol, 100 cc. causing a loss of ·001 gm. KCl.

PbO. The Estimation of Lead Oxide.

If the fusion method be employed for the analysis of a lead glass it is advisable to keep the upper portion of the crucible cool and to employ a somewhat lower temperature. The subsequent procedure for the separation of the silica is the same as with glasses which are free from lead but owing to the sparing solubility of lead chloride it is preferable to use boiling water for the washing of the silica. The solution is rendered only just acid with hydrochloric acid and a slow

current of sulphuretted hydrogen passed through the solution; the lead sulphide is filtered off and washed with cold water saturated with sulphuretted hydrogen. The lead sulphide is next dissolved in dilute nitric acid and a measured volume 2-5cc. of sulphuric acid added, the whole is now evaporated until copious fumes of sulphuric acid are evolved and on cooling water is added to produce a solution of N/1-N/2. The lead sulphate is filtered off after a few hours and washed with dilute sulphuric acid and is finally ignited and weighed in a porcelain crucible, any lead which has been reduced during the process being converted to sulphate by treatment with dilute nitric and sulphuric acids.

The addition of alcohol does not lead to more accurate results and is not recommended.

The Estimation of Sulphuric Anhydride. SO_3

The process has been fairly completely outlined on p. 32. To avoid the risk of possible contamination with silica it may be desirable to evaporate to dryness once and remove the bulk of the silica. A blank analysis must in all cases be made on the reagents and particular care must be taken in making the initial fusion to avoid the presence of sulphurous gases. The fusion should therefore be made in an electrically heated furnace.

The Estimation of Chloride. Cl.

The aqueous solution of the fusion is treated with dilute nitric acid silver nitrate is added and the whole digested on the water bath until all the silver chloride is coagulated. On allowing to stand overnight the precipitate is filtered and washed with water faintly acidified with nitric acid. It is convenient to use an asbestos packed tube for the filtration having previously dried and weighed at 180°C. Owing to the possible contamination of the first precipitate it is always advisable to re-dissolve the mass in dilute ammonia and to make a second precipitation, the first filtration in such a case is therefore preferably made through paper owing to the

possible attack of the ammonia on the asbestos. Care must be taken to avoid contamination with hydrochloric acid fumes and a blank test must be made.

As_2O_3. Sb_2O_3.

The Estimation of Arsenic and Antimony Oxides.

These elements must be determined on a separate portion of the glass owing to the volatility of the chlorides which would result in an almost complete loss of the former and a partial loss of the latter on evaporation with hydrochloric acid for the estimation of silica.

A recent paper by Allen and Zies, J. Am. Ceramic Soc., Vol. 1, No. 11, on the role played by arsenic in glasses contains some valuable data on the estimation of arsenic in its two forms of oxidation. The following method is recommended by them for the estimation of the total arsenic.

Fuse 1 gm. powdered glass with 3 gms. sodium carbonate and about 0·1 gm. potassium nitrate. When cool, set the crucible in a 12 cm. casserole, add water, cover and put in 10cc. 1 : 1 sulphuric acid. Warm until the fusion cake is removed, clean and remove the crucible and evaporate til white fumes appear. Heat somewhat longer until the silica becomes dense enough to filter without trouble; cool, add hot water and boil till any insoluble sulphate settles satisfactorily. Filter with suction, wash a few times with boiling water, and *suck dry*. The filtrate may be kept down to 100cc. For fear the bulky precipitate may retain a little arsenic, open the filter and transfer the precipitate to a 20cc. platinum crucible with the aid of a stout platinum wire, add a little sulphuric acid and 5 cc. hydrofluoric acid and evaporate to white fumes. Cool, transfer the residue to a small beaker with a little hot water, boil and filter, adding the filtrate to the principal one. To the filtrate from the silica add a fragment of potassium iodide, heat and precipitate the arsenic with hydrogen sulphide. The precipitation is materially accelerated by the reduction of the arsenic acid by hydriodic acid. When the precipitate has well coagulated, cool partially in order that the solution may absorb some

excess of hydrogen sulphide, stopper and set aside. If the solution is filtered immediately the results are likely to be too low. If the glass contains lead the precipitate will generally have an orange colour, but the colour is due to the presence of a little sulphide of lead. If the sulphate solution is allowed to stand before treatment with hydrogen sulphide till the lead is completely precipitated the sulphide precipitate is a clear yellow. After standing overnight the arsenic sulphide is filtered and washed with hot water acidified with sulphuric acid. The sulphide is treated on the filter with a few cc. of strong ammonium hydroxide and the flask rinsed with the same. If any residue is left it is transferred to a 150cc. becker and digested with ammonia and a little carbonate. The soluble portion is added to the principle arsenic solution and oxidised by hydrogen peroxide 3-5cc. of 3% solution is sufficient. Cover the beaker and boil for some time on the hot plate to complete the oxidation and decom-
with the same. If any residue is left it is transferred to a 150 cc. beaker and digested with ammonia and a little ammonium carbonate. The soluble portion is added to the principle arsenic solution and oxidised by hydrogen peroxide 3-5 cc. of 3 % solution is sufficient. Cover the beaker and boil for some time on the hot plate to complete the oxidation and decompose the excess of peroxide. When the ammonia has been expelled and the solution reduced to 10-15cc. about 7cc. 1 : 1 H_2SO_4 is added and the boiling continued about 15 minutes. If sulphur or sulphide is precipitated when the acid is added, the oxidation is of course incomplete. The arsenic is determined by the Gooch and Browning method (Am. Jr. Sci., 3, 40, 66 (1890). Dilute the solution to 100 cc., mark on flask, and add about 0·3 gm. potassium iodide, which is sufficient for small amounts of arsenic. The two-bulb trap used by Gooch and Browning is set in the neck of the flask, and the iodine is expelled by vigorous boiling. A stream of carbon dioxide led in through a capillary tube prevents bumping and aids in driving out the iodine which the solution retains tenaciously. After evaporation to 40 cc., 25 cc. more water are added, also another fragment

of potassium iodide to ensure complete reduction, and boil down again to 40 cc., repeating the operation till the solution is colourless. Then dilute quickly with cold water to 75 cc. and cool completely. Pour in 12-14 cc. of saturated solution of potassium carbonate. The final neutralization is completed by solid sodium bicarbonate. Add starch paste and titrate with iodine at a temperature of 20-25° C., below these temperatures the reaction is considerably retarded. The iodince solution contains 1·1 g. per litre.

Sb_2O_3. The Estimation of Antimony Oxide.

It is very rarely that arsenic and antimony are present together in glasses; if they are, however, the above procedure would require modification. The following method is perhaps most convenient for such occasional analyses. The mixed sulphides are dissolved and oxidised as above, and the arsenic is determined by the modification of Levol's method as given on page 36. The filtrate is acidified, and the antimony precipitated as sulphide. This is dissolved in boiling hydrochloric acid and potassium chlorate, reduced with sulphur-dioxide, after removal of the chlorine, neutralised with sodium bicarbonate, finally adding a slight excess, and when cold, titrating with iodine. As was noted on p. 35 in the case of lead glasses the sulphate of lead is liable to carry down antimony, any sulphate found should, therefore, be examined and any antimony found, determined.

Modifications of Above Scheme for Approximate Results for Purposes of Works Control.

It is convenient where time is of prime importance to estimate the bases on one or more separate portions by decomposing with hydrofluoric and sulphuric acid as outlined on p. 8, and to use only sufficient sulphuric acid to provide a slight excess which can be readily eliminated by gently heating. Sufficient must, however, be present to ensure the complete elimination of fluorides since these, especially in the determination of alumina, are a cause of trouble.

The solution of the residue in hydrochloric acid may be used for the most accurate work, or it may be used for an approximate analysis suitable for works control. The silica must, of course, for either purpose be determined by means of a fusion.

For the purpose of controlling the mixing of a batch, one or more estimations will suffice, and these will comprise silica, lime, lead, and less frequently alumina. With the small constituents owing to the necessity of accuracy in their estimation no short cuts to an approximate result would be of the least value, and these constituents will not again be considered.

Silica. SiO_2

The fusion is conducted as outlined previously, but the decomposition with hydrochloric acid may be commenced sooner, and the evaporation hastened by heating over a burner or radiator as suggested by Hillebrand (loc. cit). The final heating should, however, be made on the water bath, and a standard time after the mass is solid be employed for continuing the heating, preferably on the water bath. The filtration is performed as given under the accurate method, but the silica is only gently burned over a bunsen burner and not heated to constant weight. By observing closely standard conditions as to times of heating it is possible to obtain a figure for the silica which is necessarily not accurate owing to a loss by employing one evaporation only, but at the same time is inclined to be high by the retention of water by the low temperature of ignition. If an accurate determination of the silica is made a correction may be applied for the deficiency noted, and in this way an approximate figure for the silica obtained. The deficiency amounts from 1-2 % calculated on the original, this should be added to the amount previously found. No great degree of accuracy can, however, be expected.

Alumina and Iron Oxide.

By precipitating the filtrate twice in the usual way it will be found that almost all the silica will be contained in the precipitate: and by fusion of the weighed precipitate with

sodium bisulphate followed by subsequent solution and evaporation to fining with sulphuric acid it is possible to recover this silica and at the same time estimate the alumina by difference.

The quicker method however if a determination of alumina be required is to employ the hydrofluoric acid method as suggested in the early portion of this section using the hydrochloric acid solution for the determination of alumina.

The Estimation of Calcium Oxide.

This constituent is very accurately and rapidly determined and in soda lime glasses serves as a useful check on the accuracy of mixing. It is by no means essential to separate alumina, if the amount present does not exceed 3%, before proceeding to the estimation of lime.

The filtrate from the silica or the hydrochloric acid solution of the hydrofluoric acid decomposition is rendered distinctly alkaline with ammonia after the addition of 5 gms. of ammonium chloride and boiled. To the boiling solution a slight excess of solid ammonium oxalate is added in small portions to avoid too rapid evolution of steam and consequent loss. The boiling is continued until the oxalate appears granular, the solution is cooled and allowed to settle for a few minutes and the precipitate filtered and washed with cold water until free from oxalate and chlorides. The filter paper is opened and the precipitate washed into a beaker with water, the filter paper is treated with hot 5% sulphuric acid and washed; while the precipitate is dissolved in hot 1·5 sulphuric acid, and directly decomposition is complete 100-200cc. hot water added to prevent the calcium sulphate crystallising out. This procedure requires a certain amount of experience and practice to perform satisfactorily. The solution heated to 60°-70°C. is titrated with a permanganate solution which has been standardised against anhydrous sodium oxalate employing as far as possible the same volume and amount of sulphuric acid.

The small amount of magnesia usually associated with lime in glasses does not introduce a serious error, but should more magnesia be present a reprecipitation is desirable.

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Contents.

Foreword.

THE report on the Erosion of Tank Blocks, contained in this Bulletin, describes a method which seems capable of providing information with regard not only to the behaviour of tank blocks in a furnace, but also to founding and melting temperatures, and to the thermal conductivity and lines of flow of the molten glass. Such information has a direct bearing on the solution of problems relating to the design and operation of furnaces, and the method seems worthy of extension and development.

The reports from the National Physical Laboratory and from the Department of Glass Technology, Sheffield University, give the results of researches which, in the main, form part of several of the comprehensive investigations instituted by the Association.

In this Bulletin, also, the Director of Research discusses a few of the problems of immediate practical importance, which have at various times been investigated.

The next issue of the Bulletin will contain a general summary of the work of the Association, in which the various pieces of research work undertaken will be reviewed, and an indication given of the main points of interest arising out of each.

F. F. S. B.

I. Investigations into the Erosion of Tank Blocks.

Abstract: A method is described of determining the rate of erosion of tank blocks while in position in a furnace in operation. Sixteen thermocouples were inserted into the interior of blocks forming the side wall of a tank and one into the bridge block. Continuous records of the temperatures of these thermocouples were obtained throughout the whole life of the tank. The rate of increase of the temperature of any couple gives a measure of the rate of erosion of the block at that point. The temperature records for several thermocouples are given and the results discussed. The use of thermocouples projecting through the tank blocks below the glass level is suggested as a practical method of obtaining the actual temperature of the glass in a suitable position in the tank.

THE length of effective service of blocks used in glass melting tanks is dependent on many factors, and while the resultant effects may be readily observed and measured, it is a matter of some difficulty to differentiate the individual effect of the various processes which take place at the surface of the block while in position in the tank. Laboratory tests have from time to time been devised in order to make comparative tests of the suitability of various materials for use in tank block manufacture. The solvent action of the batch on the block and the physical changes which take place when the block material comes in contact with melting batch or molten glass can be sufficiently well determined.

It is, however, impossible to reproduce in a laboratory test the exact conditions which exist in the furnace. The block may be subject to considerable mechanical strain when in position in the tank. Strains may be set up on the surface, the magnitude of which will depend on such factors as the thermal conductivity, the emissitivity, the coefficient of expansion of the blocks, and the temperature of the glass in contact with it. This

temperature will in turn depend not only upon the flame temperature, but also on the thermal conductivity of the molten or semi-molten glass or batch, and on the direction and rate of movement of the glass, and will obviously vary from one part of the tank to another. The block may also be subject to abrasion by the flowing glass. If mechanical strains are set up on the surface, the power of the block to withstand such abrasion may be considerably altered. Cooling of the outside of the tank blocks is frequently adopted in order, presumably, to produce on the inner surface of the block a layer of chilled glass to protect the block from such abrasive action, but no evidence has been available as to the effect of such cooling on the inner surface of the block.

Information on all these subjects is desirable, not only in connection with the production of the most efficient type of tank block, but also in relation to the correct design and method of operation of furnaces. With a view to obtaining some information on the various points under discussion a preliminary investigation was undertaken and a description is now given of the method adopted and the results obtained.

The method consists of the measurement of the temperatures of the interior of the tank blocks in different parts of the furnace. This is effected by inserting metal thermocouples in holes drilled to a known depth in the blocks and thereby obtaining a measurement of the difference between the temperature of the interior of a block in one position, and that in another position, and the difference in the temperature of a point within the block at various intervals of time. With thermocouples so placed, erosion of the block surface is virtually equivalent to bringing the thermojunction nearer the source of heat, and the time rate of increase of temperature of the thermocouples gives a measurement of the rate of erosion of the block, provided the tank temperature is not materially altered throughout the period of observation. Thus the rate of erosion of the various blocks while in actual service can be compared. The temperature records may provide information with regard also to the relation between the rate of erosion of the block and the temperature, or the variations in temperature, to which it has been submitted.

If the thermocouples are suitably placed, these temperature measurements, in conjunction with the temperature of the furnace as measured in the ordinary way, may give indications as to the direction of the lines of flow of metal in the tank and the rate of conduction of heat through the glass in the various stages of melting.

The investigations were carried out at the works of one of the members of the Association who afforded us facilities for inserting thermocouples into several tank blocks in an oil fired furnace which was being used for the melting of white bottle glass. It was intended to insert all the couples to a depth of 7 inches in the blocks, which were 8 inches thick, but, as the furnace was lit before the thermocouples were fixed in position, it was in some cases impossible to insure that the thermocouples penetrated the blocks to the correct depth. Continuous records of the temperatures of the various thermocouples were obtained throughout the whole life of the tank. The investigations are not by any means exhaustive, but they provide instructive results which show that the method, modified and extended in directions indicated by the results, could be utilised with advantage in the further elucidation of several of the problems referred to.

Location of Thermocouples.

Three holes were drilled into each of four blocks in the top course on one side of the furnace and one hole in the blocks immediately below these. There were thus four series of four thermocouples each. The top thermocouple of each series was fixed about 4 inches below the flux line, the second and third vertically below that, each separated from the one above it by a distance of 6 inches. The fourth thermocouple was fixed in the block below, at a distance of about 12 inches from the third, and was thus about 6 inches from the bottom glass level. One series (B) was arranged at a distance of about 7 feet from the bridge wall, while the others, C, D and E, were fixed so that there was a distance of about 7 feet between the adjacent series of thermocouples. C and D were thus nearest the middle of the furnace, while E was about 18 inches from the doghouse end. The diagram (Fig. 1) shows the position of the thermocouples in the side wall of the furnace. The thermocouples of

each series were numbered 1, 2, 3 and 4, respectively, reading from the top downwards.

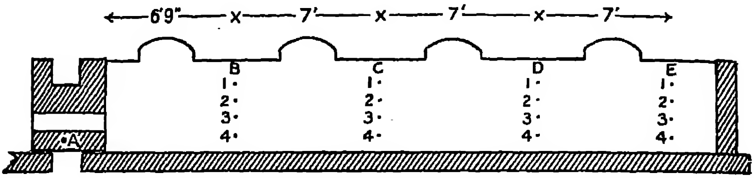


FIG. 1.

The blocks were 24 inches high by 18 inches broad, by 8 inches thick. The holes were 7 inches deep and the thermocouple junctions, when initially fixed in position, were thus separated from the glass within the furnace by one inch of block. Platinum platinum-rhodium thermocouples were used. The wires forming the couple were threaded through double-bore fireclay insulating tubes which were inserted into the holes in the block, the tubes being fixed in position by means of alundum cement. The ends of the couple were welded to compensating leads and connected to terminals on a distribution board near the end of the furnace. This board, which served as a "cold junction," was wrapped round with insulating felt to prevent sudden changes of temperature due to air currents, etc., and its temperature was measured at regular intervals. Cables were then led from the terminals on the board to the temperature recording instruments. In the centre of the bridge block, which was 12 inches thick, a hole about 9 inches deep was drilled from below and a platinum thermocouple (A) was fixed in the usual way and connected to the distribution board and thence to the recorder.

Temperature Records.

The furnace was lit on the 6th October, and melting was commenced on the 11th. The attached chart shows the temperature variations of several of the thermocouples from the 19th October to the 16th April of the following year, the furnace being put out on the 19th April. For the first 18 days and again from the 12th to the 30th September, no measurements were obtained of the cold junction temperature. The thermocouple

temperatures for the rest of the period have been corrected for the variations of temperature of the cold junction. It will be seen from the chart, that, with the exception of the three bottom curves, all the temperatures recorded show a general tendency to rise throughout the period till the end of the fifth month. There are, of course, diurnal variations. A noticeable rise is recorded on nearly all thermocouples just prior to the Christmas holidays. The increase in temperature about 25th January, when many of the temperatures attain a maximum, is significantly followed by a leak in the furnace. The application of air-cooling to the outside of the tank blocks results in a drop in temperature in all the thermocouples on 26th November. Unfortunately no information is available as to the temperature actually within the furnace as measured in the ordinary way. We, therefore, cannot tell how closely the variations in the temperature shown in the chart follow the variations of the temperatures as ordinarily measured within the furnace. Thermocouple C 4 shows no permanent increase throughout the whole period, the average temperature recorded being about 875° C. D 3 being near the surface of the block is distinctly affected by the application of the cooling air, but after the end of the second month there is a gradual rise from about 650° to 800° C. Thermocouple A, in the bridge block, shows a gradual increase in temperature during the first six weeks, no permanent increase being recorded thereafter. The temperature curves for these three thermocouples follow one another very closely and indicate the secular changes in the general temperature of the glass in the tank and can be used as datum lines to which the other curves can be related.

The readings obtained on the 19th October, that is, one week after melting had commenced, gave the following temperatures :—

A	... ... 920° C	D 1	... ... 900° C
		D 2	... ... 940° C
B 1	... ... 1000° C	D 3	... ... 790° C
B 2	... ... 990° C	D 4	... ... 1000° C
B 3	... ... 965° C		
B 4	... ... 1000° C	E 1	... ... 1090° C
		E 2	... ... 1050° C
C 1	... ... 1070° C	E 3	... ... 1025° C
C 2	... ... 990° C	E 4	... ... 835° C
C 3	... ... 1045° C		
C 4	... ... 875° C		

Thermocouples B 3, D 4 and E 4, were accidently broken during the installation of the air cooling plant, and on account of their position it was impossible to replace them. Consequently, no record was obtained of the temperature in these positions throughout the period of the experiment.

The holes in the top block in the D position had become stopped before the thermocouples were inserted. An attempt was made to re-drill the holes, but this was unsuccessful, the block apparently having become partially fused near its inner surface. These couples were therefore inserted only to the following depths in the block :—

D 1, $4\frac{1}{2}$ inches ; D 2, $5\frac{1}{2}$ inches ; D 3, $3\frac{3}{4}$ inches.

By taking the temperatures of the outer surface of the block in the D 1, D 2 and D 3 positions, and the temperatures of these three thermocouples at the specified distances within the block, we get the temperature gradient throughout the block, from which we can calculate the temperature at a point

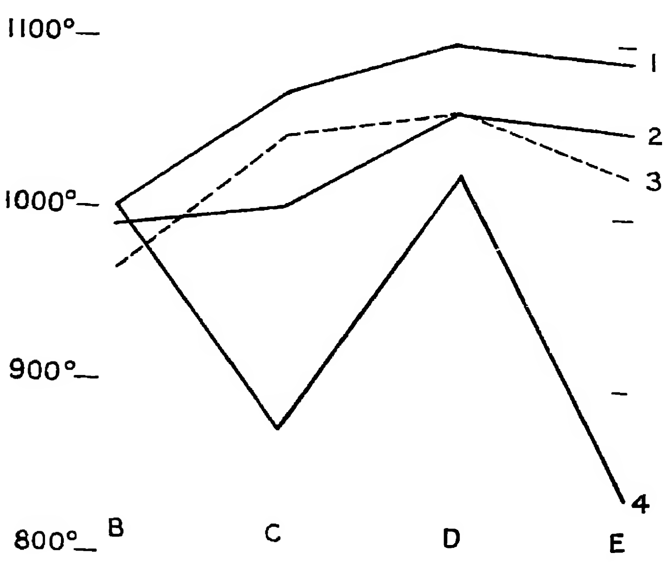


FIG. 2.

7 inches from the outer surface. These corrected temperatures are :—

D1	1100° C
D2	1060° C
D3	1060° C
D4	1020° C

The diagram (Fig. 2) shows the temperature distribution along the wall of the furnace near the glass as given by the thermocouples eight days after melting had commmenced. The corrected values for the D series are used. It will be seen that the recorded temperature of B 1 is the same as that of B 4, higher than that of B 2 and B 3. D 2 is the same as D 3. In other cases the temperatures diminish with increasing depth below the surface of the glass. C 4 seems lower than might be expected. This thermocouple may not have been inserted to the correct distance, but no measurement of its depth was obtained.

The Effect of Cooling the Outer Surfaces of the Tank Blocks.

Before discussing the rate of erosion of the blocks as evidenced by the increase of the temperatures of the thermocouples, it may be well to consider one or two of the other factors affecting variation of temperature.

As has already been mentioned, an air cooling system was installed shortly after the furnace had been lit, air being blown on to the surfaces of the blocks from pipes distributed over the bottom and side wall of the tanks. Measurements of the temperature of the outer surfaces of the tank blocks were obtained by the use of base metal thermocouples. A thermojunction was pressed against the outside of the blocks close to the points occupied by each of the thermocouples B 4, C 4, D 4 and E 3, and covered with fireclay, which on drying held the thermocouple in position. These thermocouples were numbered for reference, OB 4, OC 4, OD 4 and OE 3. The application of the cooling air resulted in an appreciable reduction of temperature amounting to about 200° C at OC 4 and OD 4. These were near the bottom of the side wall, and it is likely that the reduction was considerably greater above these positions. The reduction in the temperature of OE 3 was not so great on account of the fact that the E thermocouples are near the doghouse, that part of the furnace being freely exposed to the air and therefore from the

commencement receiving a considerable amount of natural cooling. So long as the air current was applied, the maximum variation from the mean temperature at these four points throughout the whole period of the observations was 15° C.

The temperatures of the outer surfaces of the tank blocks in the neighbourhood of the other thermocouples were also measured by the use of a base metal thermocouple. The metal at the junction was flattened and the wires then bent into the form of a " U." The junction was then pressed hard against the tank block and kept in that position until a steady reading was obtained on the indicator to which the thermocouple was connected. The following temperatures were obtained for the positions indicated :—

B 1	240° C	C 1	210° C
B 2	190° C	C 2	190° C
B 3	—	C 3	110° C
B 4	120° C	C 4	100° C
OB 4	170° C	OC 4	105° C

D 1	240° C	E 1	150° C
D 2	210° C	E 2	130° C
D 3	160° C	E 3	100° C
D 4	140° C	OE 3	120° C
OD 4	100° C		

Owing to the position of the air cooling pipes it was not possible to obtain a reading in the neighbourhood of the thermocouple B 3 or in the E 4 position. It was found that differences of temperature occurred on the outside of tank blocks on account of part of the block being screened by girders, etc., and so not being exposed to a free current of air. For example, the temperature given above for the E 2 position (130° C), was measured by placing the junction on the block at a point immediately above where the E 2 thermocouple was let in. The compensating lead of E 2 prevented the cooling air from coming directly into contact with that part. Immediately below the compensating wires, the temperature of the block surface was 40. A similar result was found in the region of the thermocouple E 3. The temperature taken at the side of this thermocouple above the compensating leads was 100° C, whereas on the side nearest the air cooling pipes, the temperature was 65° C. The relatively high temperatures recorded by the " O " thermocouples result from these thermocouples being covered with fireclay, whereas

the thermocouple in any of the other positions was simply pressed against the block and was thus exposed to the atmosphere.

An examination of the chart shows that on the 26th November when the air-cooling became effective, there is a general drop in all the temperatures, the drop being greatest on those near the bottom of the tank. The B thermocouples seem to be the least affected. This may have been due to the cooling air not being uniformly distributed. The drop in the temperature of the outer surface of the block in the B position was not so pronounced as in the C or D positions, where the following reduction of temperatures was obtained :—

C 1	25° C
C 2	60° C
C 4	90° C
E 1	80° C
E 2	60° C
E 3	70° C
D 1	50° C
D 2	30° C
D 3	110° C

The greatest drop recorded is that in D 3, a result which was to be expected since this thermocouple is only inserted 3¾ inches into the tank block.

The temporary increase in the temperature of D 3 on 17th January is largely due to the cutting off of the cooling air after a slight leak had occurred in the tank. An important point emerges from the study of the temperature records D 1 and D 2. D 1 is fixed at a distance of 4½ inches, and D 2 at a distance of 5½ inches from the outer surface of the block. A temperature of about 1200° C. is obtained by D 1, after the block had been about 4½ months in service, and by D 2 after two months' service. This increase in temperature is due to erosion of the inner surface of the tank block which obviously continued until the end of the experiment when the temperature recorded by the thermocouples was about 1350°, while the block had been reduced in thickness to about 2 inches in the pockets formed in these positions. The figures show that in this part of the tank where the inner temperature is necessarily high, the cooling of the outer surface of the tank blocks, even when they are

very thin, does not produce anything in the nature of a layer of chilled glass sufficiently viscous to prevent abrasion or erosion.

Relation between Output and Temperature.

A curve showing the daily output of glass from the tank is given at the bottom of the chart. By comparison with the temperature curves it will be seen that, in general, as the output diminishes the temperature increases, and inversely. The variation in output is largely responsible for the variation in temperatures recorded. If we take, for example, the minimum points on the output curve, the output having been diminished on account, probably, of a temporary stoppage of one of the machines, it will be seen that there is a distinct rise in the majority of the temperature curves. Such points are shown on 1st November, 29th November, 31st January, 31st March. Maximum points on the output curve as, *e.g.*, 3rd November, 16th November, 24th November, 21st December, 23rd January, 11th February, coincide generally with a fall in the temperature curves. The relation is, of course, not exact because the amount of heat applied to the furnace is not constant, efforts usually having been made to adjust the heat to the output so as to maintain the temperature within reasonably constant limits.

During the course of the experiments no attempt was made to utilise the readings given by the thermocouples to control the temperature in the tank. For this purpose, the pyrometers ordinarily in use were employed.

The relation between temperature of the glass and output is much more close in certain positions in the furnace than in others. It is very close in the E position, as was to be expected, since the amount of batch put in is regulated by the amount of glass drawn off. It is not quite so clearly defined in the C position, but is fairly close in the D position especially towards the end of the experiment when D 1 and D 2 are sufficiently close to the glass to be readily affected by temperature changes in the glass. Thermocouple B 1 does not appear to be readily influenced by changes in the amount of glass being drawn through. The temperature here is high and melting is generally complete before the glass reaches this point. The temperature of B 2 however,

shows quite a close agreement with the output. The relation is occasionally reversed, as for example when the temperature of the tank is purposely increased in order that a greater output of glass may be available. This effect may be seen on the curves at about the 21st January. The increase in temperature prior to the increase in output results in a noticeable rise of nearly all the thermocouples, especially those near the bridge. This increase, however, is not maintained by the thermocouples near the doghouse, the temperatures of which become lowered in consequence of the increased amount of batch being melted.

Thermocouple A which was fixed in the bridge block is also influenced by variations in output, but the effect is not so pronounced. The heat applied to A is derived from the glass which is passing through the bridge. If the machines are stopped and no glass is drawn through, the temperature of A drops, as the glass in the bridge begins to lose heat. If the temperature of the glass before entering the bridge remained constant, the temperature of A would rise and fall with the quantity of glass going through. We have seen, however, that the temperature of the glass in the tank is frequently allowed to rise when output is diminished, and the increase in temperature of the glass going through the bridge is more than sufficient to counterbalance the lowering of temperature in the bridge on account of the diminished amount of glass. The result is that in practice diminished output is generally followed by an increase of temperature in the bridge block and inversely.

Local Temperature Variations.

Towards the end of the second month thermocouples E 1 and E 2 show regular half-hourly changes of temperature on account of the reversal of the direction of the flames. The effect is observed also in E 3, but to a much less extent. These changes become evident when the thermocouples are no longer lagged with the layer of block which initially protected them, and are thus more sensitive to variations in the temperature of the glass in contact with the blocks.

From an examination of the E thermocouple charts, it was ascertained that the difference in temperature caused by a reversal was about 19° C in the E 1 position, 15° C in the E 2

position, and 7° C in the E 3 position. By taking points on the chart where a temperature change was sufficiently pronounced, it was possible to determine the length of time taken for this change to be recorded on the lower thermocouples. Thus a change in E 1 was followed about seven minutes later by a change in the same direction in E 2, and in about 22 minutes in E 3. That is, an increase in temperature on the surface of the glass causing an increase in a thermocouple 4 inches below the surface, takes about seven minutes to affect a couple 10 inches below the surface, and 22 minutes to affect a couple 16 inches below the surface.

Nearer the centre of the furnace, in the position of the D 1 thermocouple, which initially had a layer of 3½ inches of block separating it from the glass, inequalities due to reversals are not evident until three months after melting had been begun. From the fourth month onwards the inequalities of temperature due to reversals are more pronounced than in the E position, the maximum variation being about 25° C. D 2 becomes affected by these periodic variations about two months after melting has begun and thereafter the variations are quite definite and persistent. At the commencement of the observations, when D 1 is farther from the inner surface of the block than D 2, temperature changes occurring in the glass are recorded by D 2 earlier than by D 1. When the block has become eroded, however, temperature changes are recorded earlier on D 1 than on D 2, the time lag being greater than for corresponding levels in the E position, where there is a greater amount of mechanical mixing caused by the insertion of batch at the doghouse.

The temperatures of D 1 and of D 2 are occasionally influenced by batch piles being pushed in the direction of that part of the tank.

Thermocouple C 1 shows signs of the reversals about three weeks after the commencement, but the variations are not so pronounced as in D 2. Not until three months after melting has been begun does C 2 show signs of the reversals, and they are not evident on C 3 until the end of the fifth month. The variations are, however, quite distinct thereafter. C 4 shows no pronounced variations.

Changes in temperature due to reversals produce no measureable change in the B thermocouples. In this position, near the bridge, the glass is more fluid than towards the melting end, and there is a greater amount of movement in the molten glass.

The temperature gradient from the surface downwards into the glass as given by the records of these thermocouples is about 10° C per inch depth in the region between E 1 and E 2, and 15° C per inch between E 2 and E 3. The recorded rate varies as the thermocouples become exposed to the glass and thus subject to convection currents. Measurements made on the 24th March in the C position show a gradient of 5° per inch between the C 1 and C 2 position, 10° per inch between the C 2 and C 3 positions, and about 28° per inch between the C 3 and C 4 position. It is obvious of course, that the gradient in any vertical plane will vary with the varying thickness of block separating the thermojunction from the glass, while the gradient in different planes will vary with the rate and direction of movement of the glass.

Rate of Erosion of the Blocks.

In order to obtain information with regard to the relative rate of erosion of tank blocks in different parts of the furnace, we may make use of the time rate of change of temperature for any thermocouple over a given period. If the tank temperature is approximately constant over that period, the change in temperature of any one thermocouple gives a measure of the erosion at that point. The relation between the rate of erosion and increase of temperature will vary with the temperature. Thus, the steeper the temperature gradient from the inner to the outer surface of the block, the greater will be the change in temperature of a thermocouple fixed in the interior of the block when a given amount is removed from the inner surface. On the other hand, the thermal conductivity or the diffusivity of the tank block increases with increasing temperature, which causes the temperature gradient in the block to be less steep in the region of higher than in that of lower temperature.

By taking the temperature of the outer surface of the block, and the temperature given by the thermocouple at a known distance from the outer surface at the beginning of the experiment while the block is still 8 inches thick, we can determine, by means of the gradient so obtained, the temperature of the glass in contact with the block at the point opposite the thermocouple. Again, by taking the temperature within the block at some later date, we can by graphical means determine the required thickness of block to give on its inner surface a temperature equal to the temperature of the glass as previously determined. The thickness thus determined will show how much of the surface of the block has been eroded up to that date.

Using this method we obtain the following information with regard to the amount of erosion which has occurred in the different positions in the side wall of the tank at the end of the first three weeks.

Thermo-couple.	Temperature at end of three weeks.	Initial Temperature.	Increase in Temperature	Approximate amount of block eroded.
C 1	1180	1075	105	1 inch
D 2	1040	950	90	·9
D 1	960	900	60	·8
E 1	1160	1070	90	·8
B 2	1050	980	70	·7
E 2	1110	1050	60	·6
C 3	1100	1050	50	·5
E 3	1060	1020	40	·5
C 2	1040	1000	40	·5
C 4	910	870	40	·5

B 1 is not given in the above table since its position was altered shortly after the commencement of the investigations. An examination of the estimated amount of block which has been removed from the inner surface up to that date shows that the rate of erosion was greatest in the C 1 position followed by D 2, D 1 and E 1, then B 2 and E 2, while C 2, C 3, C 4 and E 3 seem to have undergone up to this date the least amount of erosion. Since 1 inch of the block in the C 1 position has been eroded, the thermocouple in this position must have come into contact with the glass at the end of the first three weeks.

Thereafter the gradient from the outer surface of the block to the thermojunction will be altered on account of the fact that the thermojunction is exposed to the glass and will be subjected to the effect of convection currents, so that the gradient method of measuring the amount of erosion cannot be extended beyond this point.

Having determined, in the manner described, the temperature of the glass in contact with the surface of the block in the various thermocouple positions at the commencement of the investigations, we can ascertain from the temperature records the date on which the various thermocouples attained the temperature of the glass at that point. Thus we can determine the length of time that elapsed before the different thermocouples came in contact with the glass, assuming that the glass within the tank at the end of that time has approximately the same temperature as at the commencement of the investigation. Using this method we obtain the following results :—

Thermocouple.	Initial thickness of block separating thermocouple from glass.	Time of Erosion of initial thickness of separating block.
C 1	1 inch	3 weeks
B 1	2 ,,	2 months
B 2	1 ,,	2 ,,
D 2	2½ ,,	2 ,,
C 2	1 ,,	2½ ,,
E 1	1 ,,	3 ,,
E 2	1 ,,	3 ,,
D 1	3½ ,,	5 ,,

These results can, in general, be confirmed by an examination of the temperature records of the individual thermocouples. At about the 29th October, that is three weeks after the tank had been lit up, there is a general increase in the recorded temperatures. This is largely due to a diminution in the amount of glass melted, the increased output from the first to the 3rd November being accompanied by a drop in temperature. C 1 thermocouple, however, does not respond to this general diminution, the high temperature attained by it about the 29th October,

being maintained approximately constant for some considerable time thereafter. We are, therefore, led to suppose that at the end of the third week the junction of thermocouple C 1 came into contact with the molten moving glass due to the part of the block originally protecting it, having been eroded or dissolved or broken away. Any further increase in the recorded temperature would then be due to the further erosion of the block. At the end of the experiment C 1 and D 1 have approximately the same temperature. By that time, as was shown by a subsequent examination of the blocks, a length of two inches of each of these thermocouples was exposed to the molten glass. We may thus assume that the temperature of the glass close to the inner surface of the block at the C 1 position is approximately the same as that at the D 1 position. When C 1 which was inserted 7 inches into the block had attained a temperature of about 1200° C, D 1 which was inserted to a depth of 4½ inches registered 940° C. The temperature of the outside of the block at the D 1 position was not determined before the cooling air was applied. The outside temperature, however, at D 4 position was 300° C, and the temperature outside D 1 would possibly be in the neighbourhood of 400° C. The gradient given by the temperature on the outer surface of the block and that at a point 4½ inches from that surface gives a temperature of about 1200° C at a point within the block 7 inches from the outer surface which is equivalent to the position occupied by thermocouple C 1. The temperature 1200° is the same as that recorded by thermocouple C 1. If the block were still 8 inches thick a temperature of about 1300° C. would be required on the inner surface in order to give a temperature of 1200° C. at a point 1 inch from its inner surface.

The former temperature is as high as that recorded by the thermocouples at the end of the test when they were immersed to a depth of 2 inches into the molten glass. These facts suggest that in the D 1 position 1 inch of block had by this time been removed from the inner surface, and since the block in the C 1 position had also been eroded to that amount, we are led to the conclusion that at a distance of 4 inches below the glass level, the blocks near the centre of the side wall of the furnace had lost one inch in thickness after three weeks' service.

Thereafter the erosion of the block in the immediate neighbourhood of the thermocouple tube would be greater on account of the glass being able to percolate between the block and the clay insulating tube carrying the thermocouple wires. As a result of the proportionately greater area of block exposed, pockets were formed in the neighbourhood of the thermo-junction. These were easily seen after the removal of the blocks from the furnace. The chart shows that the temperature of D 1 rises rapidly and continuously during the fourth and fifth months, and towards the end of the fifth month the temperature recorded by it is the same as that of C 1, which suggests that at that time both thermocouples are freely exposed to the glass, and that by the end of five months 8½ inches of the blocks in this region and at that level had been eroded or dissolved.

Thermocouple B 1 became accidentally displaced on the 23rd October, and could not be reinserted to its original depth, but was fixed about 6 inches into the block. The temperature recorded by it in the early stages of the experiment was, therefore, lower than at a point 7 inches within the block. Thereafter until the end of December the rate of increase of recorded temperature is more rapid than that of any of the other thermocouples, suggesting a more rapid rate of erosion of the block in that neighbourhood. This may have been partly due to the block being more readily attacked by the glass than the other blocks. By the fourth month, however, the temperature of thermocouple B 1 is higher than the average temperature attained by any of the other thermocouples on the same horizontal level at the end of the investigations, when they were exposed to the glass. These facts, together with the evidence afforded by the other B thermocouples, including B 4 which was in another block, suggests that the temperature of the glass here is higher than it is nearer the doghouse, in the C, D or E positions. This is to be expected since less heat is absorbed in this position for the melting of the glass. B 1 thermocouple probably came into contact with the glass when the temperature of the furnace was increased on 16th December, that is about 10 weeks after lighting.

During the early stages of the experiment thermocouple B 2 shows a higher temperature than B 1. This is due to B 1 not being correctly placed. The rate of increase of temperature of thermocouple B 2 during the first two months is not so rapid as that of thermocouple B 1. It rises, in common with the other thermocouples, about the middle of December, and by the middle of the third month records a temperature greater than the top couple in the E position and probably became exposed after three months service.

The temperature recorded by thermocouple D 2 rises very rapidly during the first two and a half months, and it seems probable that the couple becomes fully exposed to the glass about the end of the second month, and that the further increase in temperature during the first half of the third month is due to the further erosion of the block allowing the thermocouple to become more deeply immersed in the molten glass. At the end of the experiment it was found that a length of 3½ inches of this thermocouple was exposed. It will be noticed that, towards the end of the experiment, D 2 has a temperature as high as any of the other thermocouples then recording, but it is occasionally exceeded by D 1. At the beginning of the experiment thermocouple C 2 records an average temperature of about 50° C lower than E 2, but this difference is gradually reduced. Towards the end of December and during the first half of January, C 2 rises rapidly in relation to the other thermocouples and the curve crosses the E 2 curve about the middle of January and thereafter the temperature of C 2 remains consistently higher than that of E 2. On the other hand, C 2 and B 2 give almost the same temperature at the start, but B 2 increases more rapidly and remains higher throughout the course of the observations until about the end of the fifth month. Although the final temperatures of B 2 and C 2 are almost the same, nevertheless at the end of twelve weeks, B 2 has attained a temperature which is only attained by C 2 at the end of the eighteenth week. These facts suggest that during the early life of the tank the rate of erosion of the B block at a distance of about 10 inches below the glass level is greater than that of the C block, while the erosion of E in the early stage is more rapid than that of C, on the same level.

In the case of the E series, the maximum temperatures recorded by the thermocouples E 1 and E 2 are lower than those of the corresponding thermocouples of the other series, and the increase in the average temperatures towards the end of the experiment over those at the beginning is not so great as the increase recorded by the other thermocouples. The temperature curves of these E thermocouples have a greater number of irregularities than the other curves. The part of the furnace in which they are inserted experiences more sudden changes than other parts on account of the constant charging of batch into the doghouse. The erosion of the blocks in this region is almost as pronounced as, though of a different character from that of blocks in other regions of the furnace, where the temperature is higher, and is no doubt influenced by these frequent changes in temperature as well as by the action of the melting batch.

Both E 1 and E 2 were exposed to the glass at the end of the experiment. While E 1 is hotter than E 2 during the early part of the life of the tank, the curves approach one another about the end of the fourth month, and thereafter E 2 registers as high a temperature as, and even sometimes higher than E 1. If both thermocouples are at this time projecting from the block, the increased temperature of E 2 may be caused by the hot layers of partially molten batch being forced down by the newly admitted batch and coming in contact with the thermocouple which is not then lagged either by block or by a layer of viscous semi-molten glass.

On the 26th October, that is about three weeks after the tank was lit, E 4 thermocouple was broken and was withdrawn from its insulating tube. It was found that the glass had percolated through the hole in the tube and along the thermocouple wires to a distance of about an inch. When the block was removed afterwards, it was found that the thermocouple tube was not exposed directly to the glass. The molten glass had probably penetrated through a crack in the block. Such a defect in any of the blocks would obviously accelerate the rate of erosion and also the rate of increase of temperature as measured by the thermocouple within the block.

Using the data obtained and also the results of subsequent examination of the blocks, we can approximately represent the regions of equal erosion of the blocks along the wall of the tank by a series of contour lines, such as are shown in Fig. 3. The severity of the attack near the glass level at about 7 feet from the bridge is indicated by the crowding together of the lines. Near the dog-house end, the attack is not so much localised at the glass level but is spread over a larger area. Thus, on a horizontal level 3 inches below the glass surface, the erosion is greater at about 7 feet from the bridge than it is at 7 feet from the melting end, whereas at 8 inches below the glass level the erosion is greater in the latter position than in the former.

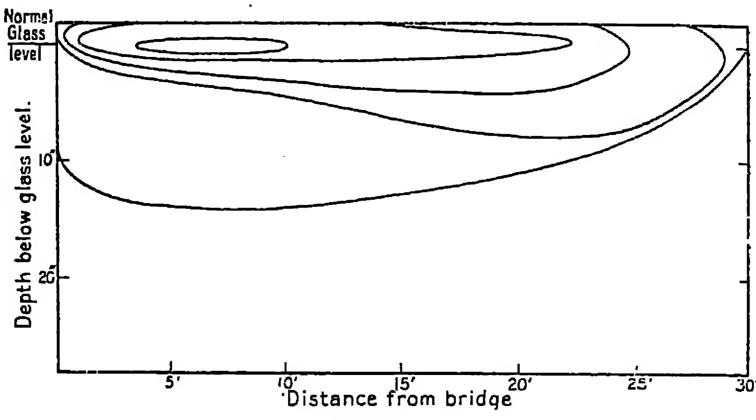
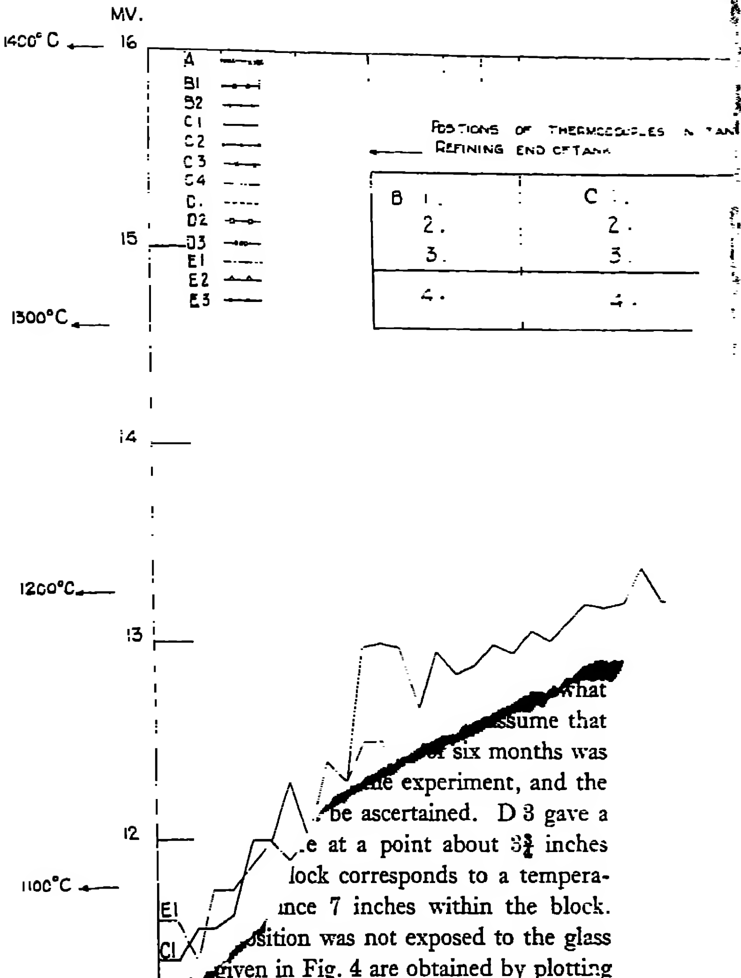


FIG. 3.

These investigations have been carried out during the life of only one tank, and it is possible that some of the temperature readings may have been affected by the particular properties of the individual blocks. We have no assurance that the blocks were uniform in their power of resistance to glass attack or uniformly free from mechanical defects. Confirmation of the results is, therefore, required by tests on other blocks. Useful information could be obtained by having three thermocouples inserted to different depths close together in one block. The necessary holes to take the thermocouples could be made after



...hat
...ssume that
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...d to a depth of 10 inches below the surface there is
... temperature as one goes from the doghouse to the D
...on, a slight fall towards the C position, and the temperature
... rises again towards the bridge.

the blocks have been moulded and dried, but before they have been fired. This would obviate the danger of partial disintegration or of cracks being introduced by the drilling of three holes close together in the fired block.

Temperatures Recorded Towards the End of the Investigations.

The average temperatures recorded by the various thermocouples towards the end of the investigations were as follows :—

B 1	... ... 1330° C	B 3	... ... (broken)
C 1	... ... 1320° C	C 3	... ... 1260° C
D 1	... ... 1350° C	D 3	... ... 750° C
E 1	... ... 1240° C		(corrected ... 1250° C)
		E 3	... ... 1180° C
B 2	... ... 1325° C	B 4	... ... 1085° C
C 2	... ... 1310° C	C 4	... ... 890° C
D 2	... ... 1325° C	D 4	... ... 1070° C
E 2	... ... 1230° C	E 4	... ... 910° C

B 1 broke at the end of the fourth month. It was then recording a temperature of about 1330° C and this temperature would probably have been increased owing to further erosion of the block. The tank temperature, however, at that time was somewhat higher than during the sixth month. We may thus assume that the temperature at the B 1 position at the end of six months was about 1330. B 3 was broken earlier in the experiment, and the temperature at that position cannot be ascertained. D 3 gave a reading of 750°. This temperature at a point about 3¾ inches from the outer surface of the block corresponds to a temperature of about 1250° at a distance 7 inches within the block. The thermocouple in this position was not exposed to the glass in the tank. The curves given in Fig. 4 are obtained by plotting these temperatures. The temperature for C 4 is not included, because the exact depth of penetration of this couple into the block is not known. The curves show that in the glass on the surface and to a depth of 10 inches below the surface there is a rise in temperature as one goes from the doghouse to the D position, a slight fall towards the C position, and the temperature then rises again towards the bridge.

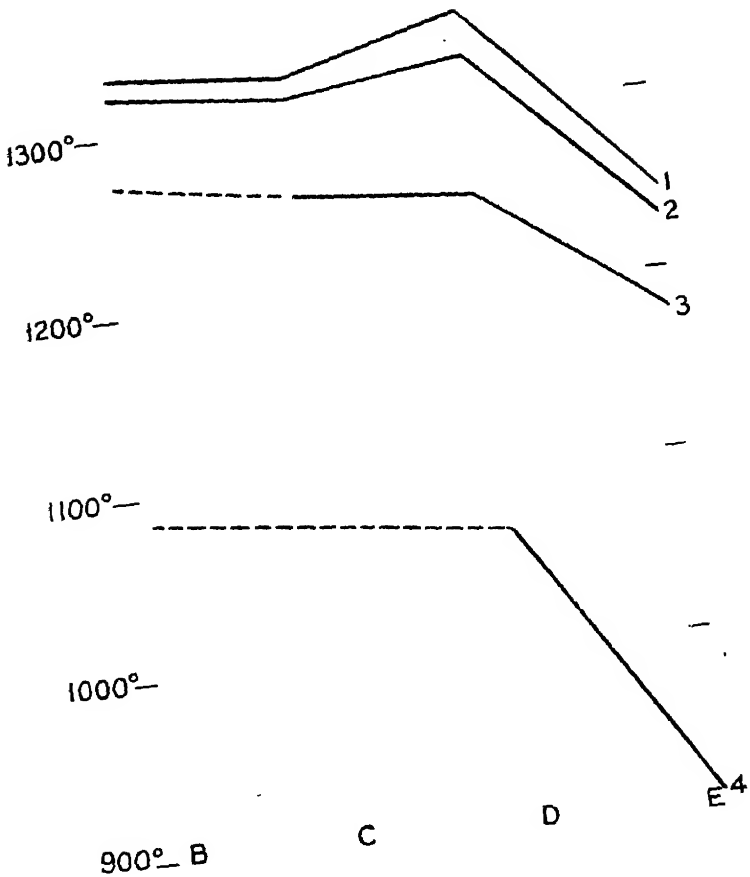


FIG. 4.

At a distance of about 16 inches below the surface the temperature gradient from the doghouse to C is much the same as at 10 inches below the surface, while there is a slight increase in temperature from C to D. At a distance of 2 feet 4 inches below the surface, the rate of increase of temperature from E to D is much greater and there is an increase from D to B. This increase is, no doubt, caused by the hot molten glass being drawn down towards the doghole in the bridge.

Fig. 5 shows the lines of equal temperature along the wall of the tank. These have been obtained by using the results referred to above and extrapolating where necessary.

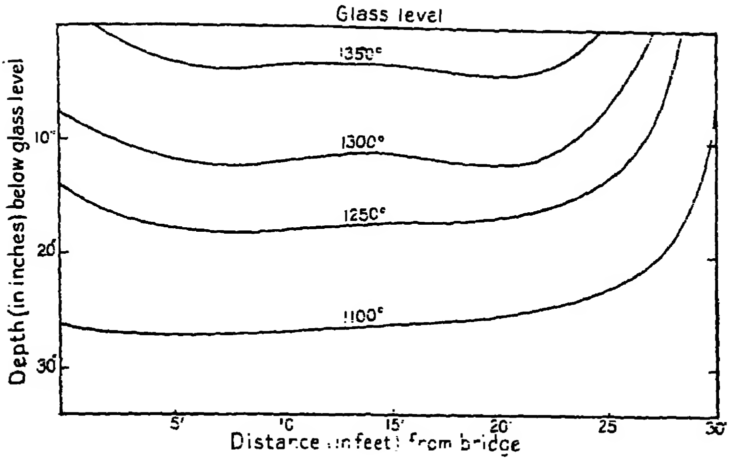


FIG. 5.

Appearance of Blocks.

An examination of the blocks after removal from the furnace showed that those in the first course were badly eroded. The thickness of the blocks at the flux line was as follows :—

B, $1\frac{3}{4}$ inches ; C, $3\frac{1}{4}$ inches ; D, 3 inches ; E, 6 inches.

Block B, which was nearest the melting end, was thinner at the flux line than the others. The temperature record of the thermocouple in this position in the B block led one to expect this, the gradient over the first three months being greater here than in any of the other positions. The surfaces of the B and C blocks showed distinct vertical channelling. Blocks D and E were more uniformly eroded ; the channelling was not so pronounced, and the surfaces showed signs of erosion through horizontal movements or swirling of the glass or batch.

In the region of the two top thermocouples on each of the blocks, pockets had been formed. The block and the fireclay insulating tube had been dissolved or eroded leaving the thermocouple exposed to the glass in the 1 and 2 positions of all the blocks. Figs. 6 and 7 are photographs showing the thermocouple wires, D 1 and D 2, projecting from the inner eroded surface of the D block.

The length of wire of the various couples that had been immersed in the molten glass was :—

	B	C	D	E
Position 1 ...	Broken	2 inches	2 inches	2 inches
Position 2 ...	1½ inches	1 inch	3½ inches	1½ inches

In none of the blocks had the thermocouples in the 3 or 4 positions come into contact with the glass. No sign of crystallisation could be observed on the thermocouple wires, and no change had taken place in their temperature - emf. relations as a result of their immersion. The failure of thermocouple B 1 was probably due to a mechanical defect in the welding, since there was no visible sign of weakening of the wires through crystallisation or solution in the neighbourhood of the junction.

The Use of Metal Thermocouples in Glass.

The durability of these thermocouples on exposure to the glass suggests that, if used in the manner described, they can profitably be applied to indicate changes in the temperature of the glass in the part of the furnace in which they are inserted and to enable the temperature of the glass within the tank to be suitably controlled. If they are adopted for such a purpose it is essential that the platinum platinum-rhodium wires be not exposed to the reducing atmosphere of the furnace. Otherwise, they will have a very short life. The position chosen for their insertion should be such as to permit of information being obtained as to the temperature of the glass in that part of the tank where it is essential that the temperature be maintained constant. Attention should also be paid to choosing a position where the attack on the block is not severe. If the block, in which the thermocouple is fixed, is rapidly eroded, there will be a rapid increase in the temperature measured by the thermocouple, and there will

also be the inconvenience of disturbing the thermocouple when the block has to be replaced. Two thermocouples were inserted into the working end of a furnace supplying glass to two Owens machines and were placed so as to give information with regard to the temperature of the glass before going into the revolving pot. These thermocouples have now been in use for over nine months, and have given satisfactory service. In the case of a flow feed machine the most suitable position would appear to be in the channel, a special pocket or baffle being made, if necessary, in the inner wall of the channel block. If the thermocouple be fully exposed to the glass at the commencement, the increase of temperature due to the erosion of the block will then be small.

Summary of Results.

The investigations have been carried out only in one tank, and the results summarised below may in some respects be influenced by the conditions peculiar to that furnace.

1. The use of air for cooling the outer surfaces of the blocks results in an appreciable lowering of the temperature of these surfaces and also, to a less extent, of the inner surfaces. There is, however, no evidence that such cooling produces a layer of chilled glass on the inner surface even when the block is only 4 inches thick.

2. The temperature of the glass in contact with the top blocks is sufficiently high to render the glass mobile and permit of convection and other currents being set up close to the surface of the blocks. These currents may cause erosion of the blocks in addition to aiding solution. The nature of the erosion of the blocks near the bridge is different from that near the doghouse, the difference being due to the different movement of the glass in the two positions.

3. Considerable variations were found to exist in the temperature of the glass from day to day, due to variations in the amount of glass being drawn off.

4. The rate of erosion of the tank blocks near the surface of the glass is extremely rapid in the early stages. Near the middle of the furnace 1 inch of block was removed from the

inner surface within three weeks after melting had commenced, about 2 inches within ten weeks, and about 4 inches before the end of the fifth month.

5. On a horizontal level about 10 inches below the surface the rate of erosion is not so rapid, amounting to about 1 inch in ten weeks.

6. At a distance of about 16 inches from the surface the rate of erosion is slow, less than 1 inch being removed during the whole life of the tank (7 months).

7. Near the glass level the block attack is most severe about seven feet from the bridge. The blocks near the doghouse undergo rapid attack during the first three weeks, but thereafter the rate of attack is slower than in other parts of the furnace.

8. The temperature of the glass near the surface is highest about midway between the doghouse and the bridge. Near the bottom of the tank, however, the temperature of the glass is highest towards the bridge end. The temperature gradient within the glass from the surface to the bottom of the tank is greatest near the doghouse, diminishes rapidly to a point about 9 feet from the doghouse, and diminishes gradually thereafter towards the bridge. The doghouse end of the furnace in this case was well exposed and consequently experienced a certain amount of cooling by the atmosphere.

9. Near the melting end a time lag of about 20 minutes occurs before a change of temperature in the glass close to the wall 4 inches below the surface is recorded at a point 16 inches below the surface in the same vertical plane. The lag is somewhat greater nearer the middle of the tank close to the wall, but it is not measurable near the bridge, where there is more rapid circulation of the glass.

10. Platinum platinum-rhodium thermocouples, when inserted through the tank blocks so as to be protected from the atmosphere of the tank, provide a method of measuring the actual temperature of the glass and so enabling control of temperature to be obtained. For use over long periods, such thermocouples should be inserted in positions where the erosion of the block is not rapid.

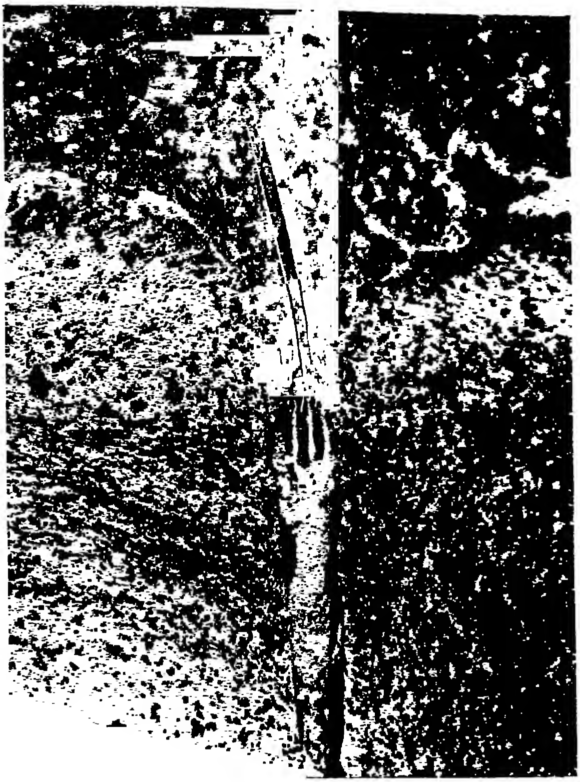


FIG. 6.

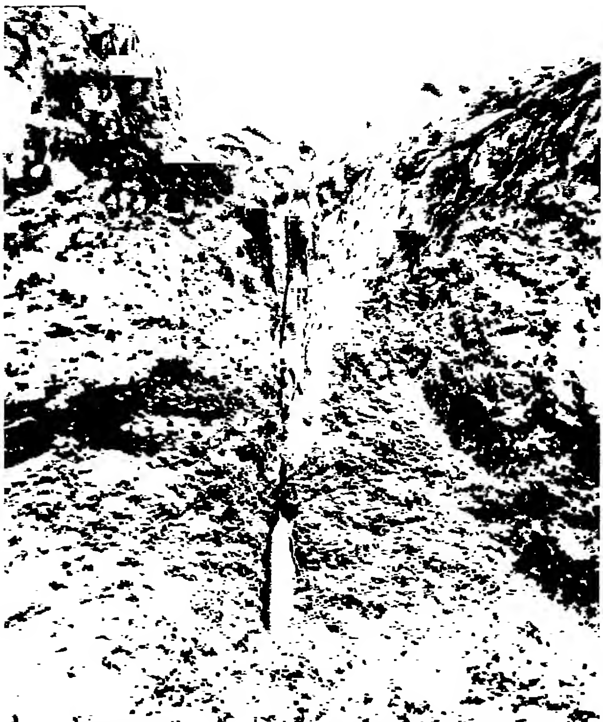


FIG. 7.

II. Viscosity—Temperature Curves of two Lamp Working Glasses.

A Report from the National Physical Laboratory to the Glass Research Association.

THE samples of glass were two of those referred to in the report on the " Experimental Production of Glasses for Lamp Working " (Bulletin, No. 12, pp. 5-22), and differed only in the form in which magnesia was introduced, dolomite being used for the glass A, and magnesia itself for the glass G.R.A. 2.

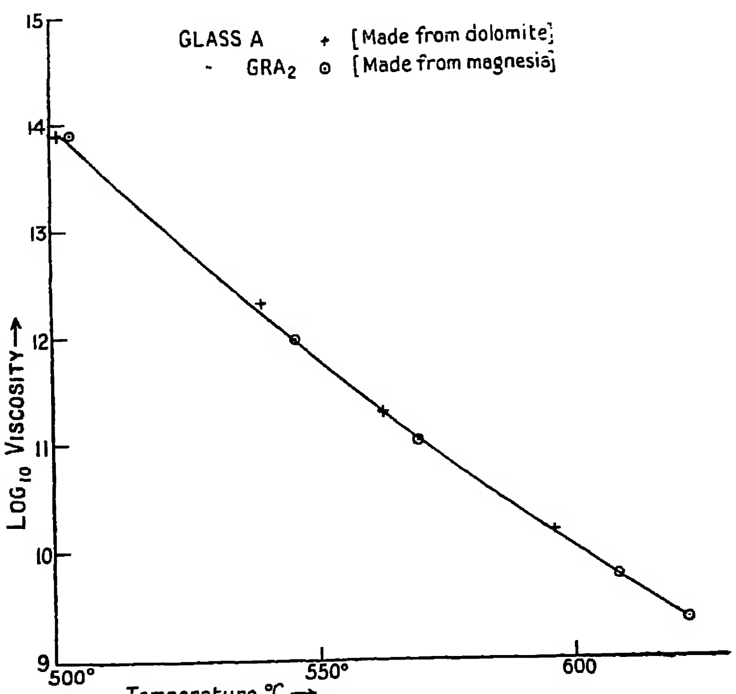


FIG 1.

The viscosities were determined in the usual way on rods of equal diameter. As, however, the diameter was slightly smaller than that usually employed, the absolute values of the viscosity may be a little in error. The comparative results are not influenced by this circumstance.

It will be seen from the attached graph (Fig. 1) that the viscosity curves of the two glasses are equal within the limits of experimental error.

The compositions of the actual rods used were found to be as follows :—

	Glass A.	Glass G.R.A. 2.
SiO_2	65·90	66·00
$Al_2O_3 + Fe_2O_3$	5·35	5·39
MnO	·22	·13
CaO	6·04	6·00
MgO	1·64	1·61
Na_2O	15·18	15·16
K_2O	5·20	5·12
B_2O_3	·45	·45
	99·98	99·86

III. The Viscosities of Soda-Lime-Silica Glasses.

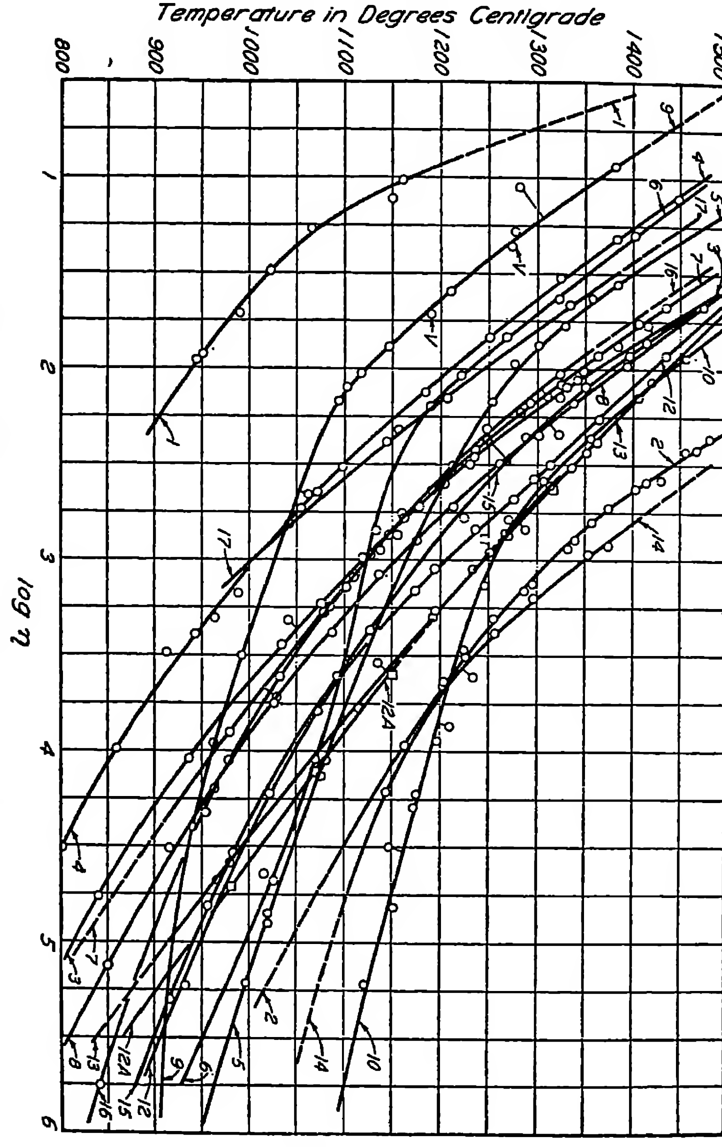
Report from the Department of Metallurgy and Metallurgical Chemistry of the National Physical Laboratory, by V. H. Stott, M.Sc., D. Turner, B.Sc.Tech., and H. A. Sloman, B.A., A.I.C., presented by W. Rosenhain, B.A., D.Sc., F.R.S.

Abstract.—The results of further measurements of the viscosities of soda-lime-silica glasses are given at various temperatures. For a temperature of 575° C. the lines of equal viscosity have been plotted against composition. It is shewn that small quantities of impurities have a large influence on the viscosity, and that the presence of such impurities leads to errors in the determination of these curves, which are considerably greater than the errors associated with the actual measurements of viscosity. Determinations by other workers are critically reviewed in order that all the existing data may be utilised to the greatest advantage.

A SERIES of determinations of the temperature-viscosity curves of a number of soda-lime-silica glasses at relatively low temperatures has been made by the Laboratory. The curves obtained are shewn in Fig. 6, and the analyses of the glasses are given on page 49. From these curves it has been possible to draw the lines of equal viscosity over a considerable field of compositions at a temperature of 575° C. These contour lines are shewn in Fig. 7. Measurements have also been made by the Laboratory of the temperature-viscosity curve of a soda-lime glass up to 1420° C. (see page 46). The measurements on this glass are discussed later in conjunction with determinations by other workers. In view of the small amount of systematic work which has been done by any workers on the viscosities of the soda-lime-silica glasses, it has been thought desirable to review all recent work on the subject, in order that the sum total of the data may be used to the greatest advantage.

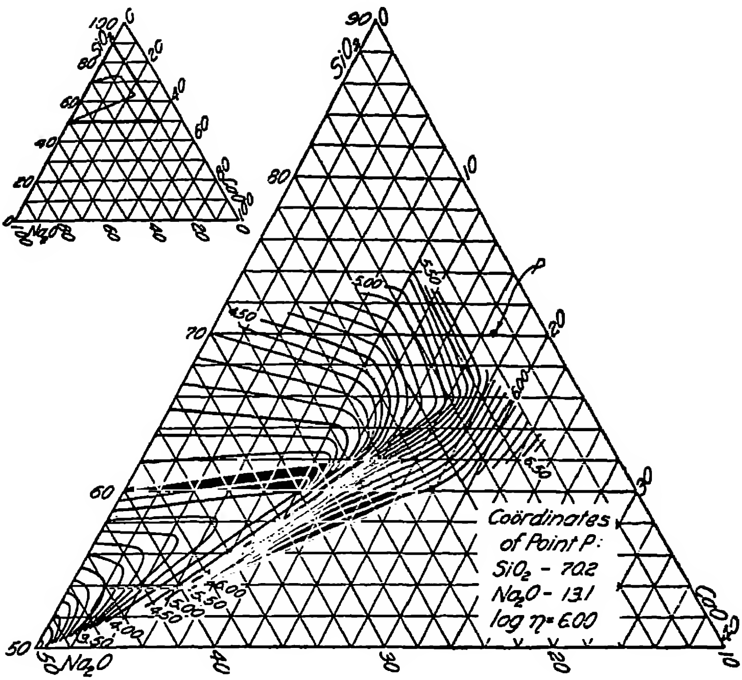
At the higher temperatures a very important series of measurements has been recently published by Washburn and

Shelton. Measurements have also been made at high temperatures by English and by the National Physical Laboratory.



THE LOG η—TEMPERATURE CURVES FOR THE GLASSES INVESTIGATED

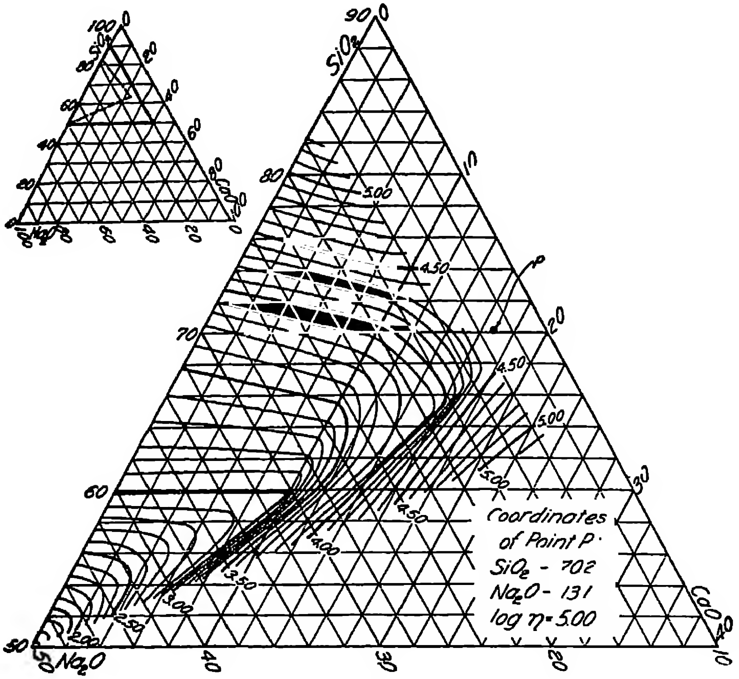
FIG. A.



LOG ISOKOMS AT 900 DEG. C.

FIG. B.

At the lower temperature the results of determinations by the National Physical Laboratory will be discussed together with the work of English in this range. Figs. A. to H. taken from Washburn's paper show the numerical results of his work. In general the method of measurement adopted appears to be satisfactory. A variation of the calibration factor of the apparatus with viscosity was found, however, to be of considerable magnitude. It was in the same direction but of greater value than that discussed on page 18 *et seq.* of the Glass Research Association Bulletin No. 8. In connection with this point Washburn and Shelton state that " the method of standardising the porcelain apparatus eliminates any possible error from such variation." It appears from the discussion just mentioned that the above statement is probably incorrect. The possible effect on the



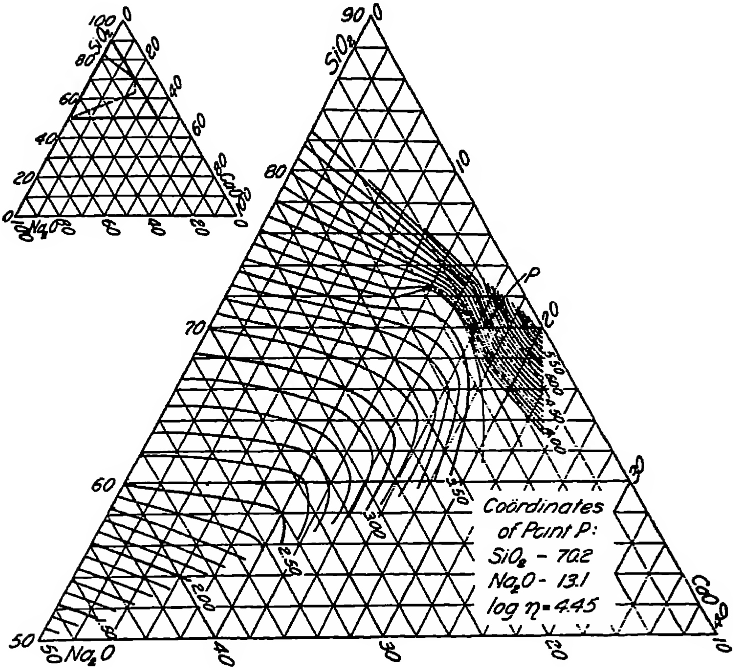
Log Isokoms at 1000 deg. C.

Fig. C.

results of uncertainty in the calibration factor will be referred to later in connection with discrepancies between the measurements of Washburn, and those of English, and of the National Physical Laboratory.

The preparation of the samples by melting mixtures of three previously prepared glasses is open to some objection, since it is not unlikely that the properties of glass depend to some extent on its mode of preparation.

The peculiar shapes of three of the curves are ascribed to devitrification. Le Chatelier supposes that irregularities in the curves for two other glasses were also due to this cause. In the tables shewing the viscosities of the various glasses at

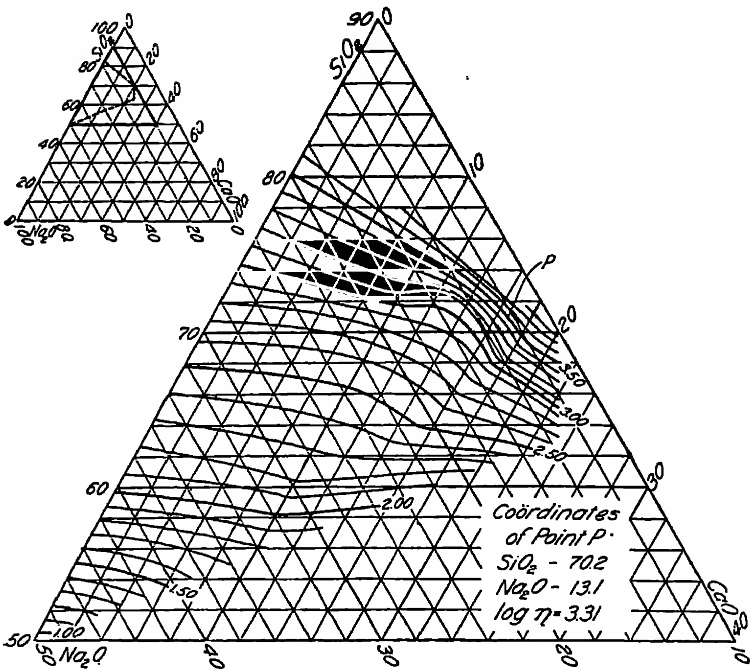


Log Isokoms at 1100 deg. C

Fig. D.

different temperatures, the values which may be supposed to be abnormal are not indicated. Moreover, in drawing the isokoms (lines of equal viscosity) the abnormal values have been used, so that at temperatures below 1200° the form of the isokoms is very different from their form above that temperature. The procedure cannot be justified from the practical standpoint that the curves allow the actual viscosities of partially devitrified glasses to be calculated, because the degree of devitrification would not necessarily be the same in different cases.

Interesting information is obtained by plotting the logarithms of the viscosities of the sodium silicate glasses against their composition. Comparison of measurements of viscosity with those of other physical properties has shewn that the

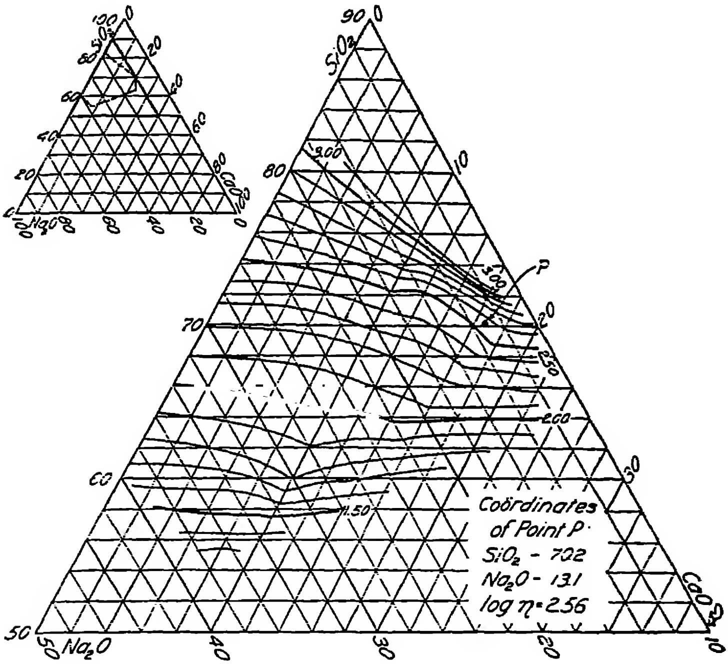


LOG ISOKOMS AT 1200 DEG. C.

FIG. E.

form of curve which would be anticipated, in the absence of molecular combinations or dissociations, would be a line approximately straight, with a slight tendency to be convex to the axis expressing composition. (The compositions should preferably be expressed in molecular percentages. Since the molecular weights of Na_2O and SiO_2 are 62 and 60 respectively, the ordinary percentage compositions have been used for convenience in Figs. 1 and 2.)

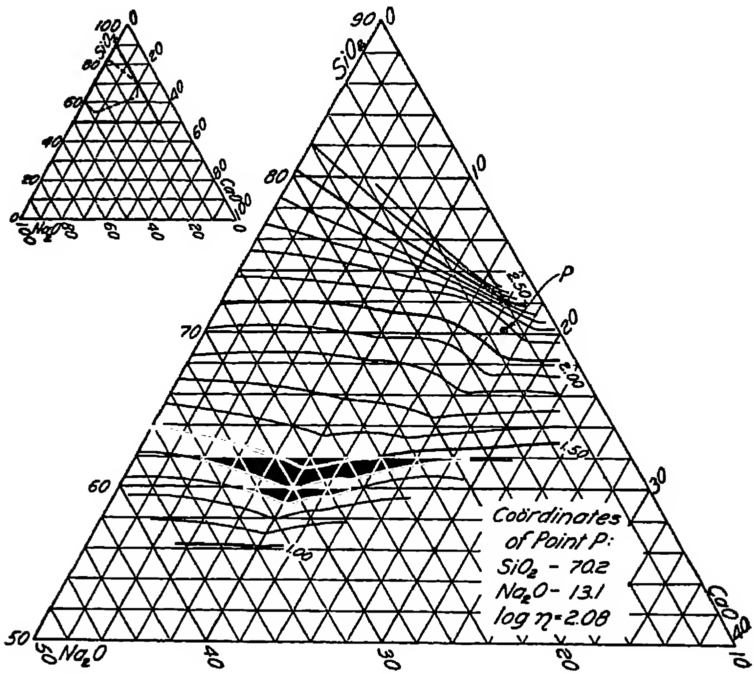
The curves for the lower temperatures in Fig. 1 cannot be drawn without a point of inflexion. It is possible, however, to place the point of inflexion between any pair of the experimental points, so that more observations are required to determine the exact shapes of the curves. The existence of a point



Log Isokoms at 1300 deg. C.

Fig. F.

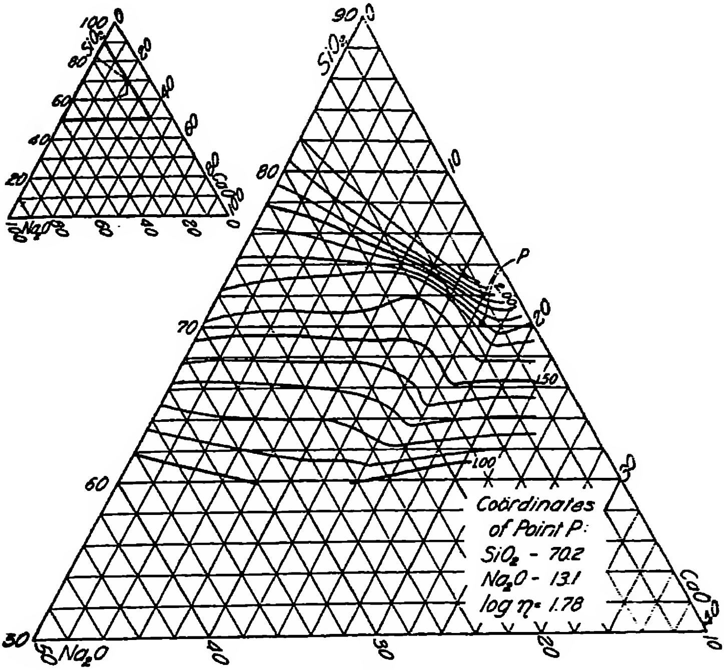
of inflexion on the viscosity curves is an indication of molecular association, although the composition of the compound is not directly determined by the position of the point of inflexion. There are substantial grounds for the belief that the composition of the compound is indicated by the point where the deviation of the actual curve from the normal type of curve is a maximum. The point of inflexion is, therefore, usually closer to the liquid of higher viscosity than the point on the curve corresponding with the composition of the compound. In the case under consideration we have knowledge of the existence, in the solid state, of a compound Na_2O, $2SiO_2$. Fig. 3 shews the specific refractions of the sodium silicates computed from the figures given by Peddle in the Journal of the Society of Glass Technology, May, 1920. It is clear that the maximum deviation of the curve from



Log Isokoms at 1400 deg. C.

Fig. G.

any curve approximating to a straight line joining the specific refractions of the end points, must be very close indeed to the composition Na_2O, $2SiO_2$, and this may be taken as evidence of the existence of the compound. The fact that such a compound exists at room temperatures affords considerable grounds for suspecting its existence at much higher temperatures, since glass, owing to its high viscosity, tends to retain, during the cooling process, the equilibrium at high temperatures. From the foregoing considerations, it may reasonably be supposed that the abnormal forms of the viscosity curves of the sodium silicates are due to the formation to some extent of the compound Na_2O, $2SiO_2$. Assuming this to be the case, the curves of Fig. 1 should



Log Isokoms at 1500 deg. C.

Fig. H.

probably be drawn with the points of inflexion somewhat higher up the curves than they appear in the actual diagram.

Fig. 2 shews the curves obtained for the glasses containing 10 per cent. of lime. The curves are of the same general type. Attempts to redraw the isokoms directly from the experimental figures obtained by Washburn have shewn that whilst the isokoms which he has drawn are not inconsistent with those figures, they are arbitrary to a considerable degree. Attention has already been drawn to the undesirability of using figures derived from devitrifiable glasses. Since seven points are required to determine adequately the form of one of the curves of Fig. 1, and since extrapolated values of the viscosities must be employed in certain cases, it will readily be conceded that a very much

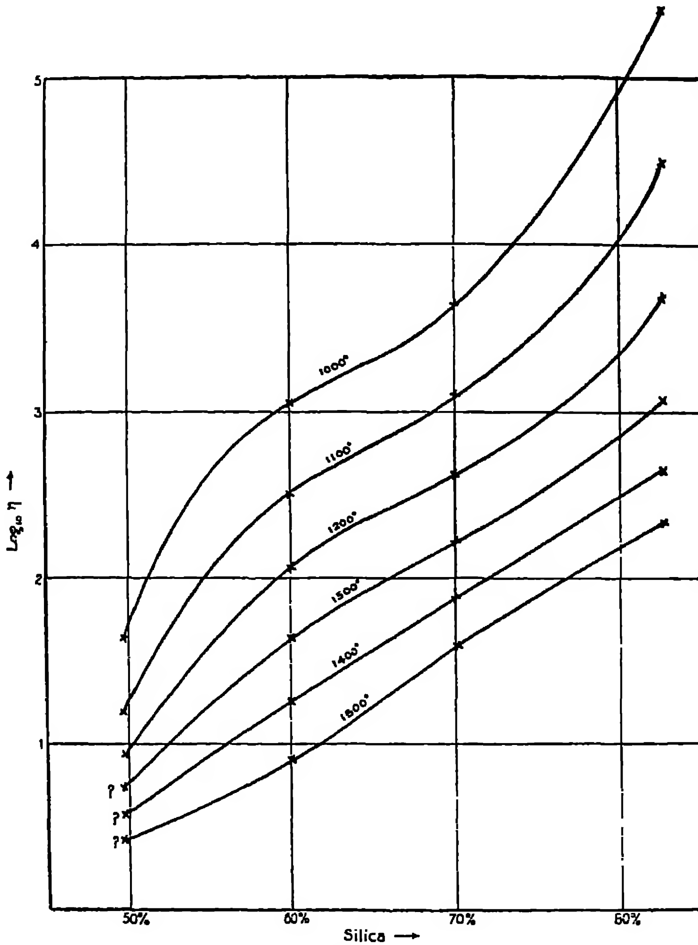


Fig. 1.

larger number of glasses than sixteen is necessary in order thoroughly to explore the field. The above remarks apply even more strongly, *mutatis mutandis*, to the measurements made by Washburn and Libman, of density and surface tension.

Washburn's tables of viscosities have given rise to an interesting generalisation by Le Chatelier who states that the variation of the viscosity of these glasses with temperature can be expressed

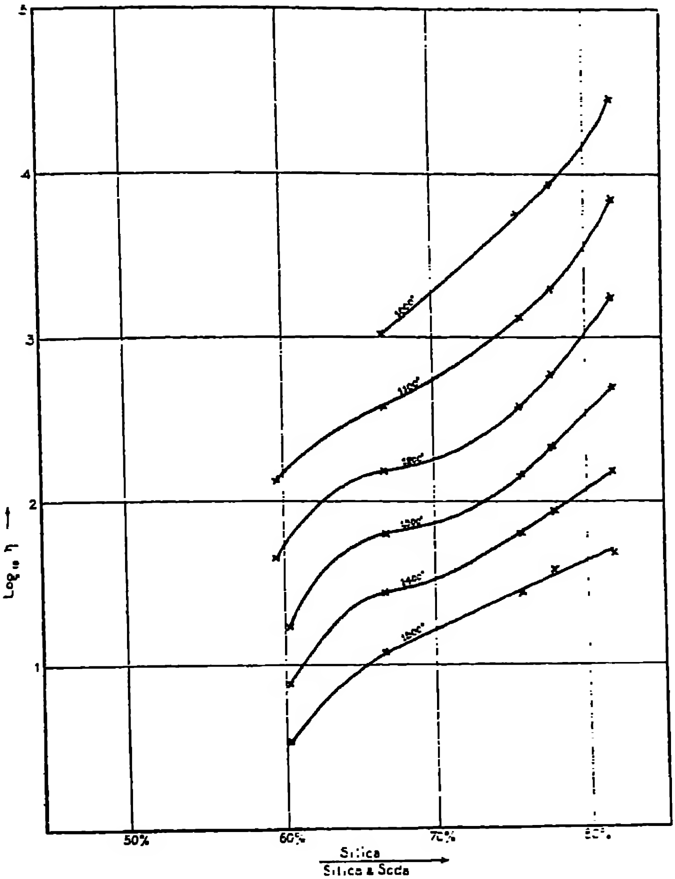


FIG. 2.

by means of 'a double exponential with only two parameters', namely :—

$$\log \log \eta = - Mt + P$$

Examination of this equation shews that its form would be changed by a change in the magnitude of the unit of viscosity. Since η and t have different dimensions, it follows that any relation between them should be expressed as an equality of two dimen-

sionless quantities. The above equation should therefore be written

$$\log \log {}^{\eta}/_{\eta_0} = -\mathrm{M}t + \mathrm{P},$$

where η_0 is a constant having the dimensions of a viscosity, M has the dimensions of the reciprocal of a temperature, and P is a number. The equation has now three parameters, not two, although the value of η_0 appears to be very close to unity for the glasses under consideration. The practical value of the equation is greatly reduced by the fact that three parameters are involved. The equation does not give a satisfactory representation of the relation of viscosity to temperature in the case of the glass St 59* between 600° C. and 1400° C. even when the most suitable value is assumed for η_0.

The particular case chosen by Le Chatelier for illustrating the agreement between the formula and the experimental results of Washburn is an especially favourable one. Up to the present no simple formula expressing the variation of the viscosity of a liquid with temperature has been found to be of general application, although many formulae are quite accurate in special cases.

A comparison is possible, in the case of one glass, between the measurements of Washburn, English, and the National Physical Laboratory. Fig. 4 shews the viscosities of the glass № 15 determined in the manner described in the Glass Research Association, Bulletin, No. 8.

The glass has the composition :

SiO_2	72·22
Al_2O_3	·71
Fe_2O_3	·11
CaO	6·94
MgO	·53
Na_2O	19·49

* *See* Glass Research Association Bulletin, No. 8, Page 23.

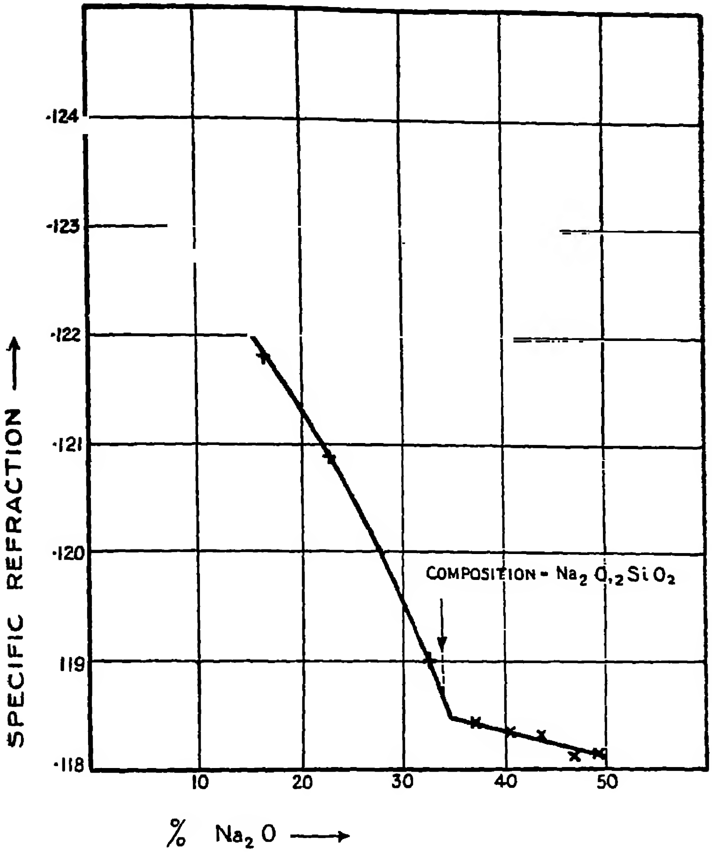


FIG. 3.

The curve marked W on the figure is obtained from Washburn's diagrams. It corresponds with a composition

SiO_2	=	72·22
Na_2O	=	19·49
CaO	=	8·29

The curve marked E is obtained from English's figures for glass 6, after applying a correction derived from Washburn's isokoms. The series of circles slightly above English's line shews the uncorrected points. As in the previous case the compositions have been calculated from the percentages of silica and soda only.

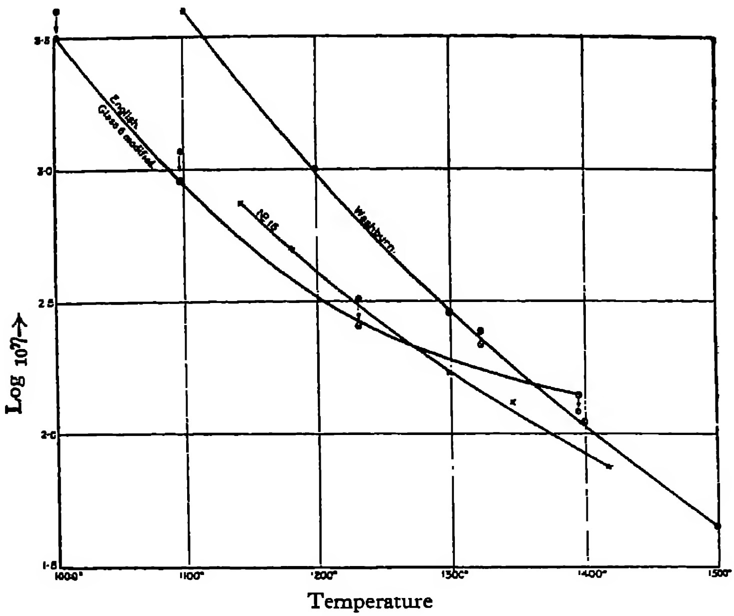
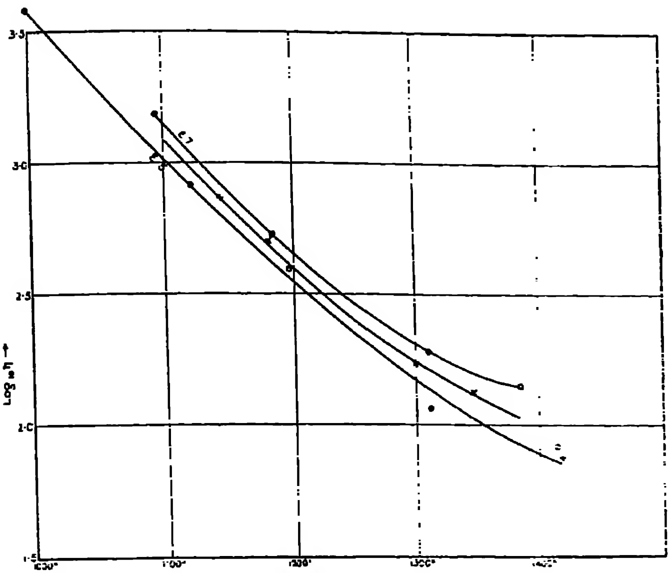


FIG. 4.

The discrepancies between the three curves are striking. The irregular nature of the last three points of English's curve suggests very serious errors. The first three points of his curve however, lie on a line nearly parallel to the Nº curve. If the last two points of his curve are each shifted back a distance of 83° parallel to the temperature axis the new curve is parallel to the Nº curve.

It appears, therefore, that either a considerable discrepancy exists between the two curves, or that there has probably been a large error at the two upper temperatures. Fig. 5 shews English's results for glasses 5 and 7. The middle curve is drawn by averaging the logarithmic viscosities shewn on the other two curves. It may be presumed to apply to a glass having a composition midway between the compositions of glasses 5 and 7. As before, at the lower temperatures the curve is parallel to the Nº curve (the crosses represent the experimental result for Nº 15), but at the higher temperatures there is some divergence. Here again, however, the measured values are very uncertain. The parallelism



Temperature

FIG. 5.

between this curve and the NP curve is a little diminished after applying the following corrections deduced from Washburn's isokoms for the small difference in composition from that of the NP glass.

at 1100°	subtract	·27
1200°		·23
1300°		·20
1400°		·16
1500°		·16

The difference between the slope of Washburn's curve, and that of English's curve, or the National Physical Laboratory's curve, is so great as to throw considerable doubt on the value of Washburn's observations, since the two latter curves have approximately the same slope. It is possible that Washburn's results are due to lack of homogeneity of his glass. Variations in the quantities of the minor constituents are not of sufficient magnitude to explain the discrepancy, and a large change is necessary in the proportions of the major constituents to alter greatly the

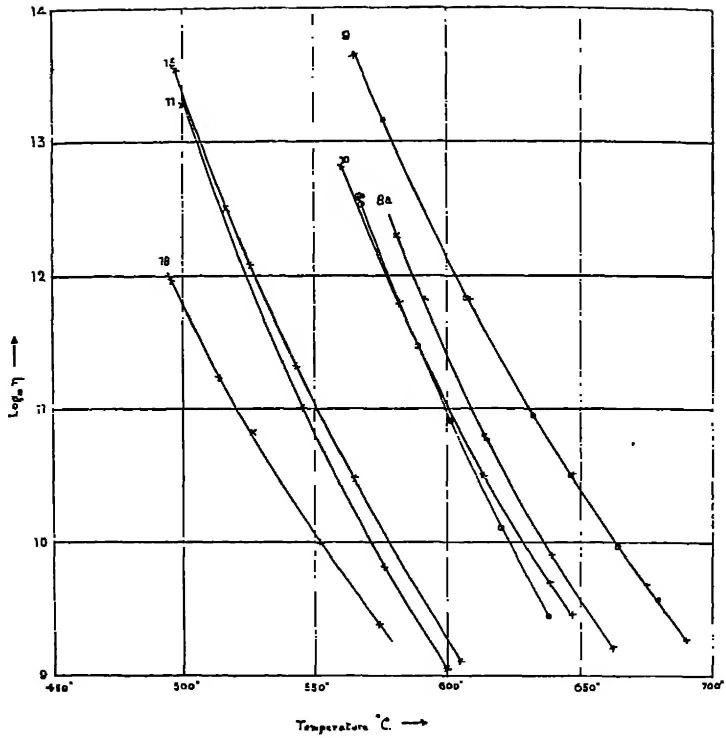


FIG. 6.

slope of the curve. (The glass in Washburn's series which has a viscosity-temperature curve closest to that of № 15, is his glass 8, containing 70 per cent. silica and 30 per cent. soda).

Reference has already been made to the variation of the calibration factor of Washburn's apparatus with viscosity. Washburn used the experimentally determined values of the calibration factor, and assumed its value to be independent of the density and chemical nature of the liquid. If we suppose on the contrary, that variation of the calibration factor depends on the nature of the calibrating liquid. (*i.e.*, the hydrodynamical properties of the liquid cannot be expressed in terms of the density and coefficient of viscosity only), a constant factor should be used in calculating the results. It is readily seen that such a method of calculation increases the slope of Washburn's curve,

and therefore increases the discrepancy between this work and that of English and of the National Physical Laboratory.

At the lower temperatures, a series of viscosity measurements on the soda-lime-silica glasses has been made by the National Physical Laboratory using the method described in Bulletin No. 2. The accuracy of the determinations has been increased by grinding the rods on a lathe to the required dimensions instead of fusing together hand drawn rods. Fig. 6 shews, plotted against temperatures the logarithmic viscosities of glasses of the following compositions.

No. of Glass.	8a	8b	9	10	11	15	18
SiO_2 ...	68·38	62·34	76·48	71·94	69·08	78·02	76·00
Fe_2O_3 ...	·22	·22	·30	·16	·29	·16	·26
Al_2O_3 ...	2·22	1·48	2·54	·54	·59	·58	·38
MgO ...	trace	·36	trace	·61	·60	·47	·64
CaO ...	14·70	18·24	9·92	12·40	8·00	6·60	1·50
Na_2O ...	14·62	17·70	10·80	14·38	21·18	20·16	21·04
	100·14	100·34	100·04	100·03	99·74	99·99	99·82

On the assumption that the viscosity is a continuous function of composition the curves of Fig. 6 enable lines of equal viscosity (isokoms) to be drawn over a considerable field at a temperature of 575° C. Corrections should be made to the compositions of the glasses in order to allow for the effects of impurities and also because the analytical figures do not total precisely a hundred per cent. Since the viscosity values are much less sensitive to a given error (as a percentage of the total weight of glass) in the amount of silica than in that of the other constituents, the errors of analysis have been considered as errors in the silica value.

Attempts were made to utilise some published and unpublished measurements of viscosities very kindly communicated by Mr. English, in order to calculate the corrections which should be made to allow for the presence of magnesia and alumina. The uncertainty of the magnitudes of the corrections was so great, however, that it was decided to draw approximate, uncorrected contour lines. The errors in the logarithmic viscosities due to neglect of the corrections are probably less than 0·4.

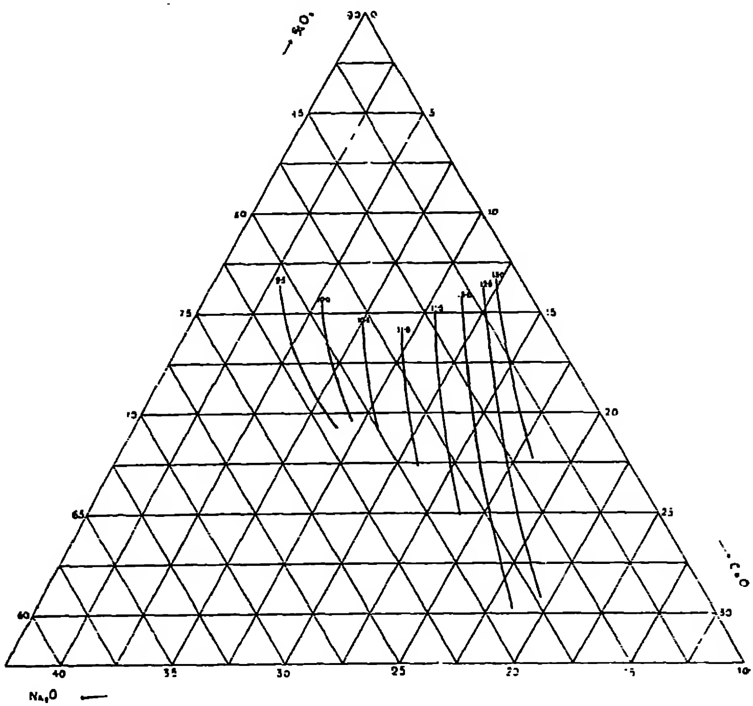


FIG. 7.

The errors in the actual measurements of logarithmic viscosities are probably of the order of 0·05 or less, so that a recalculation of the contour lines would be desirable if, at a future time, accurate values of the correction terms were available. The contour lines are shewn in Fig. 7. A comparison is possible between viscosities read from the diagram, and the viscosities determined by English on a series of soda-lime glasses, each containing approximately 74·5 molecules per cent. of silica. After making small corrections to English's figures by means of the contour lines (since the percentages of silica are not quite exact), it is found that the curves obtained in each case, by plotting logarithmic viscosity against percentage of lime, are roughly parallel.*

* In calculating the absolute values of the low temperature viscosities English has confused the coefficient of viscous traction with the coefficient of viscosity. His published results at low temperatures are, therefore, three times the true values. The necessary corrections have been made in the graphs given in the present report.

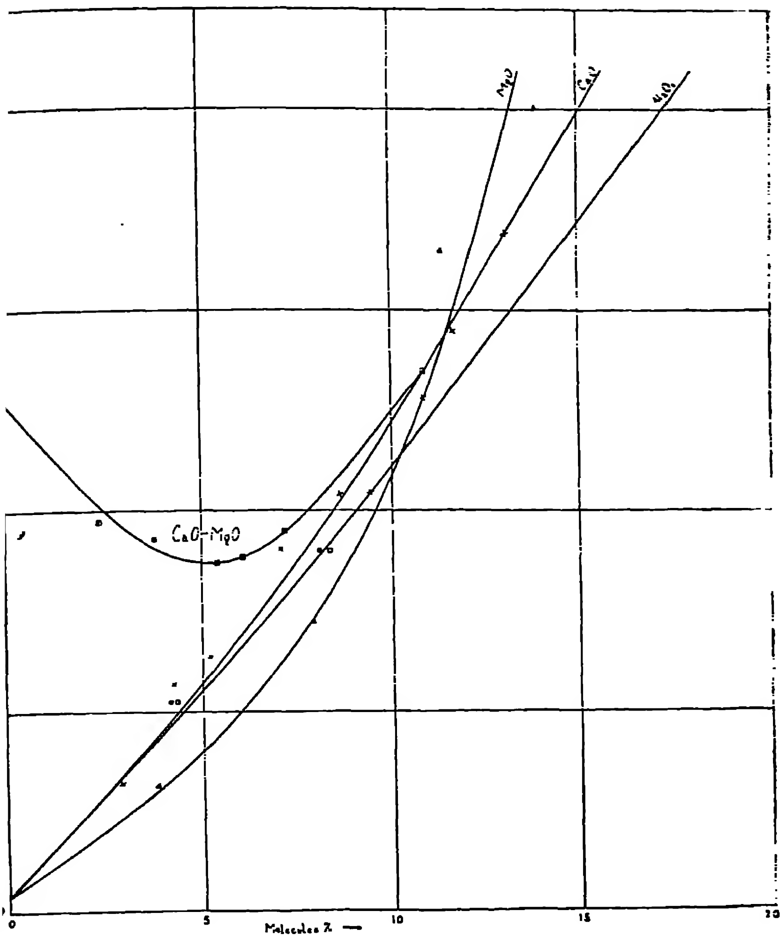


FIG. 8.

The greatest variation in the distance between the two lines measured in the direction of the axis of logarithmic viscosities is ·35. This difference is probably due to the neglect of the corrections for alumina and magnesia. The variation was reduced to ·10 by the use of rough corrections derived from English's work by a method of successive approximations. This figure might have been still further reduced by a repetition of the calculation.

Fig. 8 shews the basis of such calculations, and indicates at the same time how uncertain such corrections are. The ordinates of the curves are logarithmic viscosities, and the abscissae are molecular percentages of lime, alumina, and magnesia respectively. The curves marked CaO, Al_2O_3, and MgO, respectively, refer to glasses derived from the same sodium silicate (containing 74·5 molecules per cent. of silica) by the equimolecular substitution of part of the soda by lime, alumina, or magnesia as the case may be. The curve marked CaO-MgO refers to a soda-lime glass in which an equimolecular substitution of magnesia for lime has taken place. In order to represent these glasses, we may employ axes in the plane of the paper for the representation of logarithmic viscosities, and molecular percentages of lime; and a third axis at right angles to the other two, for the indication of the molecular percentage of magnesia. The curve for the magnesia-soda-lime-silica glasses then lies in a plane inclined at 45° to the plane of the paper, and it is the projection of this curve on to the plane of the paper which is shewn in the diagram. The points on the various curves have been corrected by a method of successive approximations for the presence of magnesia, lime, and alumina, where these substances occur as impurities. Although these corrections are uncertain, their effect on the argument which follows is nil, as their complete omission produces an effect on the curves which is very much smaller than the irregularities due to other experimental errors. The lime curve has been rendered more regular by correcting, where possible, the compositions from the contour lines, so that the points refer to glasses which are strictly members of the series intended. In this case also, the changes due to the corrections are much smaller than other errors. Let us consider the soda-lime-magnesia-silica glasses, and let us suppose for the moment, that a given addition of a component to a glass affects its viscosity in a manner dependent on the viscosity of the original glass, but not on its composition. It may be deduced from this supposition, that the curve CaO-MgO is symmetrical, and that its slope, where it meets the CaO curve, is equal to the difference of the slopes of the CaO and MgO curves at that point. A similar deduction applies to the other end of the CaO-MgO curve. The curves of Fig. 8 have been drawn to satisfy these conditions, and they pass

ery satisfactorily between the experimental points. The hypothesis is, therefore, not in this case inconsistent with the experimental evidence available. (It is obvious from the contours that the hypothesis is not true in general). It was hoped that by extending the hypothesis to the case of the alumina glasses, the desired corrections might be made to the contours. The Al_2O_3 curve was drawn from knowledge of three points at the lower end, and of the slope of the curve at a logarithmic viscosity of about 12, derived by combining the above hypothesis with two results, kindly communicated by Mr. English, of measurements on soda-lime-alumina-silica glasses. The two points indicated by filled-in circles are plotted without correction. The two circles alongside are the corresponding points corrected for the fact that the compositions of the glasses differ from the theoretical ones, by assuming that the contour lines of the system soda-alumina-silica have the same directions as those of the system soda-lime-silica (the curves Al_2O_3 and CaO not being very greatly different). It is manifest that the three curves MgO, CaO, and Al_2O_3, require to be determined with a very high accuracy indeed, if it is desired to deduce corrections from them accurate to say, 0·1 on the logarithmic viscosity, a precision probably considerably less than that of our measurements on the soda-lime-silica glasses. It may, indeed, be stated that the glasses on which measurements of viscosity at relatively low temperatures are to be made, will have to be prepared from materials of known purity, melted without contamination, if it is wished to obtain final results in which the errors due to impurities, or inaccurate compositions generally, are not considerably greater than the errors of the viscosity determination itself. The use of special laboratory melting apparatus would naturally preclude the melting of large pieces of glass, and it is probable that the Margules method of measuring viscosities described on page 11 of Bulletin No. 2 would be found the most convenient. The necessity for extremely accurate centring of the inner cylinder (which does not arise when the shape only, of the viscosity-temperature curve is to be determined) is a very considerable, though doubtless, not insuperable obstacle.

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"Sur la Viscosité du Verre," Le Chatelier. Comptes Rendus, No. 11, Vol. 179. 15th September, 1924.

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V. The Effect of Cullet on the Melting and Working Properties of Potash-Lead Oxide Glasses.

Report from the Department of Glass Technology, University of Sheffield, on investigations carried out on behalf of the Glass Research Association.

Abstract: As in the case of soda-lime glasses, so also with the potash-lead oxide glasses, retardation of the rate of melting takes place as the proportion of cullet added to the charge is increased, the retardation becoming noticeable when the proportion of cullet is 50 per cent. or more. The retardation does not necessarily apply also to the rate of refining. Glasses melted from mixtures containing more than 50 per cent. of cullet frequently became free from seed sooner than those melted with smaller cullet proportions. Fine seed developed at a late stage of the founding process in several glasses melted at 1400°. The viscosity and rate of setting increased with increasing proportions of cullet, especially when 50 per cent. or more of cullet was used in preparing the glass.

IN a previous report* the effect on the melting and working properties of a typical soda lime glass due to the incorporation in the batch of varying proportions of cullet has been discussed. The rather unexpected result was disclosed, namely, that the inclusion of more than 40 per cent. of cullet in the batch did not hasten, but rather retarded the melting and refining of the glass. The well known effects of increasing proportions of cullet in hardening the glass at the working temperature and of shortening the working range were confirmed, although analysis of the finished glasses showed that there was no loss of sodium oxide as a result of the remelting of that proportion of the glass which was included as cullet.

In the case of potash-lead oxide glasses, with which the present report deals, the question of the influence of the cullet

* Glass Research Association Bulletin 12, pp. 48-57.

added is still more important in the sense, that a much larger proportion is used than is customary in melting the soda-lime glasses.

The type of glass studied was one which we have used as standard in investigations on potash-lead oxide glasses, the batch being composed of sand 900, red lead 600, potash 300, potassium nitrate 48, manganese dioxide 1. All the materials were used "dry," which really means, in view of the slight moisture content of the sand and red lead, and the rather varying content of the potash (2·5 per cent to 8 per cent. was found in different samples), that the batch would contain between 1 and 2 per cent. of moisture.

From this batch a quantity of cullet was prepared from fully refined and plained glass by drogading. The broken glass was passed through a wooden screen with ½-in. holes, the pieces which did not pass through being subsequently crushed and re-sieved.

With the batch and the dried cullet, two series of meltings were carried through, one at a temperature of 1350°, and the other at 1400°.

The Batch and Cullet Proportions Investigated.

In both sets of melting, quantities of 100 lbs. and 50 lbs. were mixed separately for each pot and filled on completely in three charges at intervals of 90 minutes. The proportion of cullet used in each of these two series of glasses is given in Table I.

TABLE I.

Per cent. Cullet in Charge.	Meltings at 1350°. 100 lbs.	Meltings at 1350°. 50 lbs.	Meltings at 1400° 100 lbs.	Meltings at 1400° 50 lbs.
0	767	767	—	—
20	768	768A	776	776A
30	769	769A	777	777A
40	770	770A	778	778A
50	771	771A	779	779A
60	772	772A	780	780A
75	773	773A	781	781A
90	774	774A	782	782A
100	775	775A	783	783A

Glass No.	Per Cent. Cullet in Charge Melted.	Weight of Charge Melted.	Melting Temp.	Proof actually batch free at	Estimated time to become batch free	Remarks on Melting.	Remarks on Refining.
768 ...	20	100 lbs.	1350°	5 hrs.	4¾ hrs.	776 was the better at 4 hrs.	Fine seed after 20 hrs.
776 ...			1400°	5 hrs.	4½ hrs.		Fine seed prevailed throughout.
768A ...		50 lbs.	1350°	5 hrs.	4¼ hrs.	Equally good at 4 hrs.	Fine seed after 20 hrs.
776A ...			1400°	5 hrs.	4¼ hrs.		Fine seed persisted and was not removed after 20 hrs.
769 ...	30	100 lbs.	1350°	5 hrs.	4¾ hrs.	769 was slightly the better melted at 4 hrs.	Fine seed after 20 hrs.
777 ...			1400°	5 hrs.	4¾ hrs.		Nearly plain between 12 and 16 hrs. Fine seed later.
769A ...		50 lbs.	1350°	5 hrs.	4¼ hrs.	Equally good at 4 hrs.	Gradual improvement throughout, but not seed-free after 20 hrs.
777A ...			1400°	5 hrs.	4¼ hrs.		Seed free at 14 hrs.
770 ...	40	100 lbs.	1350°	5 hrs.	5 hrs.	778 was much better than 770 at 4 and 5 hrs.	Nearly plain at 16 hrs; free from seed later.
778 ...			1400°	5 hrs.	4½ hrs.		
770A ...		50 lbs.	1350°	5 hrs.	4½ hrs.	778A was slightly the better at 4 hrs.	Fine seed after 20 hrs.
778A ...			1400°	5 hrs.	4¼ hrs.		Slow improvement throughout, but never seed-free.
771 ...	50	100 lbs.	1350°	6 hrs.	5¼ hrs.	Not quite batch-free at 5 hrs.	Very minute seed at 20 hrs
779 ...			1400°	5 hrs.	4¾ hrs.	Quite batch-free at 5 hrs.	Better at 16 hrs. than at 20 hrs.
771A ...		50 lbs.	1350°	5 hrs.	4¾ hrs.	779A was better than 771A at 4 hrs.	Fine seed after 20 hrs.
779A ...			1400°	5 hrs.	4½ hrs.		Slow improvement throughout, but never seed-free.
772 ...	60	100 lbs.	1350°	6 hrs.	5¼ hrs.	Practically alike at 5 and 6 hrs.	Nearly seed-free at 20 hrs.
780 ...			1400°	6 hrs.	5¼ hrs.		Free from seed at 16 hrs; little seed at 20 hrs.

TABLE II. (continued).

Glass No.	Per Cent. Cullet in Charge Melted.	Weight of Charge Melted.	Melting Temp.	Proof actually batch free at	Estimated time to become batch free.	Remarks on Melting.	Remarks on Refining.
772A ...	60	50 lbs.	1350°	5 hrs.	$4\frac{3}{4}$ hrs.	780A was better than 772A at 4 hrs.	Distinctly seedy after 20 hrs.
780A ...			1400°	5 hrs.	$4\frac{1}{2}$ hrs.		Nearly seed-free at 16 hrs; fine seed at 20 hrs.
773 ...	75	100 lbs.	1350°	6 hrs.	$5\frac{1}{4}$ hrs.	Practically the same at 5 hrs. and nearly plain at 6 hrs.	Very little seed from 14-20 hrs.
781 ...			1400°	6 hrs.	$5\frac{1}{4}$ hrs.		Nearly seed-free at 16 hrs., not so good at 20 hrs.
773A ...		50 lbs.	1350°	5 hrs.	5 hrs.	About the same at 4 hrs. but at 5 hrs. 781A was slightly the better	Little seed at 20 hrs.
781A ...			1400°	5 hrs.	5 hrs.		Continuous but slow improvement throughout.
774 ...	90	100 lbs.	1350°	6 hrs.	$5\frac{1}{4}$ hrs.	Not quite free at 5 hrs.	Very little seed from 14-20 hrs.
782 ...			1400°	5 hrs.	5 hrs.	Just free at 5 hrs. ...	Fine seed persisted throughout.
774A ...		50 lbs.	1350°	6 hrs.	$5\frac{1}{4}$ hrs.	782A was the better at 4 and 5 hrs.	Little seed at 20 hrs. Fine seed persisted throughout.
782A ...			1400°	5 hrs.	5 hrs.		Seed-free after 10 hrs.
775 ...	100	100 lbs.	1350°	—	—	783 had less seed than 775 at 5 hrs.	Practically plain from 16 hrs. onwards.
783 ...			1400°	—	—		
775A ...		50 lbs.	1350°	—	—	783A was rather less seedy than 775A at 4 hrs. and 5 hrs.	Seed-free after 10 hrs.
783A ...			1400°	—	—		Very fine seed persisted throughout.

Observations on the Melting Process.

Before being charged, the pots were brought up to the melting temperatures, namely, 1350° for the first series and 1400° for the second series, and after being charged were again raised to these temperatures as quickly as was consistent with safety. It was noticed that with those batches which had the larger proportions of cullet, the pots always took longer to attain once more the melting temperature after the charging was complete. In fact, when 75 per cent. or 90 per cent. of cullet was present, and the melting temperature was 1400°, practically all the raw materials of the batch had melted by the time the charge as a whole had melted down and the pot attained the standard temperature.

After the third charge had been added, proofs were taken at the end of each hour to determine how melting was proceeding until the glass was perfectly free from unmelted batch. From the appearance of these proofs, the time after the end of the first charge, at which the glass became batch-free was estimated, and the results are tabulated in Table II.

During the melting process there did not appear to be any strongly marked differences in the rate of melting of these glasses; all melted down quite easily, and at the end of one hour after the addition of the last charge they contained no lumps of unmelted batch, but only isolated solid particles, while at the end of two hours after the last charge the glasses were entirely free from unmelted batch except some of those prepared from 50 per cent. or more of cullet.

In general, it may be said that the addition of 20 per cent., or of 30 per cent. of cullet did not appreciably alter the rate of melting either at 1350° or 1400°; but further increase in the proportions of cullet did cause gradual lengthenings of the time necessary to melt all the batch.

The causes at work may be similar to those which we indicated when discussing the results of tests on soda-lime-silica glasses. But as, to our knowledge, no study of the reactions involved between potash-lead oxide and silica have been made of

a type similar to those of Cobb and of Niggli on the soda-lime-silica series, we are driven back for an explanation to a discussion of what we observed during the melting operations.

It has already been mentioned that glasses with the lower proportions of cullet always attained the temperature of the furnace after filling-on quicker than did those with higher proportions of cullet. This may possibly be due to a slower rate of heat penetration through the cullet than through the actively melting batch, and also to the fact that melting batch causes movement among its parts and thus carries heat by such motion, in a manner somewhat similar to convection. The slowness of the transference of heat from the sides of the pots to the body of the glass was particularly noticeable in the meltings with 90 per cent. of cullet, in which cases one hour after the last charge was added the glass round the sides of the pot was quite soft and well melted, whilst that in the middle of the pot was distinctly hard and contained a considerable proportion of unmelted batch.

A further observation that may help to explain the longer time that was required for the melting of those glasses containing large proportions of cullet was that they only softened slowly as melting proceeded, while those which were melted from large proportions of raw material became completely fluid much quicker even though they contained at the time some particles of undissolved silica. The process of melting glass from batch, as indicated in the report on soda-lime glass, appears to be a dual process involving the formation of a mobile glass with a low silica content, followed by the solution of the remaining silica, thereby increasing the viscosity.

In the case of melting cullet, there is no stage at which a mobile glass is formed at comparatively low temperatures, and it is, therefore, necessary to raise the temperature considerably to get it completely molten. In the melting operations this difference was not very noticeable until the glass with 50 per cent. of cullet was being melted, and as the cullet was increased beyond this amount the effect became more and more pronounced, so much so that those mixtures with 75 per cent. and 90 per cent. of cullet were almost, if not quite, free from batch by the time

the whole of the cullet had become completely fluid, at 1350° or 1400° as the case might be.

Two other points arise out of a consideration of Table II., namely (1) the difference in time required to obtain the various meltings free from unmelted batch in the two sizes of pots was from one-quarter to one-half an hour, and was probably due to the fact that the 50 lbs. pot with its larger ratio of surface area to glass content, always rose to the temperature of the furnace after filling quicker than did the 100 lbs. pot.

(2) The times required for the complete melting of similar glasses at 1350° and 1400° respectively, were not very different. Where there was a difference, naturally the quicker melting took place at 1400°, but, judging by the number of meltings in which no increased rate of melting was observed, there appeared to be very little, if any, advantage in carrying out the melting of these glasses at a temperature higher than 1350°.

The Influence of Cullet on the Rate of Refining.

The process of the refining of these glasses was tested by taking proofs at the end of 12, 14, 16 and 18 hours after the addition of the first charge, and by examination of the glass on working, which was always begun at 20 hours after the addition of the first charge. The results of these observations are included in Table II.

Considering first the meltings at 1350°, it appeared that in general the glasses with 50 per cent., or more of cullet in the batch became free from seed rather more quickly than those with less than this amount, whilst the end member of the series, namely the glass prepared from 100 per cent. of cullet, became seed-free in ten hours, or in only half the time that was allowed for the normal founding period. No 770, with 40 per cent. of cullet melted in a 100 lbs. pot, appeared to be an exception, and no explanation can be offered to account for this abnormally low figure. Paradoxical as it may seem, in general, those mixtures which were quickest in melting were most difficult to obtain free from seeds.

In those glasses which remained seedy the full length of the normal period of 20 hours, there always appeared a gradual but slow improvement in the quality of the glass during the last eight hours in the furnace, and it appeared likely that if a longer time could have been given, they might have become quite plain. In these cases the seeds were always very small; so small, in fact in some cases, that they could not easily be detected until the glass had been drawn into rod or tubing.

Turning now to the meltings carried out at 1400°, in no case was the glass perfectly seed-free after being in the furnace for twenty hours. In every case as the melt became free from batch, there was developed a fine seed with just a few larger bubbles. These larger bubbles were removed fairly easily, but the fine seed persisted, especially in those meltings containing the smaller proportions of cullet. In the 100 lbs. meltings, those with 20 per cent. to 50 per cent. cullet were distinctly more seedy when worked, than those containing 60 per cent. or more of cullet, while the 100 per cent. cullet glass was nearly free from seed when it had been in the furnace for 16 hours, and this comparative freedom from seed persisted till the glass was worked out.

In the case of meltings from mixtures containing 30, 40, 50, 60 and 75 per cent. cullet, made in the 100 lb. pot, the glasses appeared to be free or nearly free from seed after about 16 hours in the furnace, but they developed fine seed before being worked out at the end of the usual 20 hours run. In the other meltings, the fine seed which developed on the melting of the batch gradually decreased, but was never removed entirely except in the case of glass No. 783 (100 per cent. cullet in 100 lb. pot). The proportion of cullet in these meltings appeared to have little influence on the rate of refining, as freedom from seed appeared to be influenced more by the development of the fine secondary seed than by anything else.

Comparing the meltings carried out at 1400° with those at 1350°, it is obvious that so far as the refining of the glass is concerned there is very little, if any, advantage in running at 1400°. In most cases the glass became seed-free,

or nearly so, quicker at the higher temperature, but unless the temperature was reduced, a secondary seed was developed which it was almost, if not quite, impossible to remove.

The Working Properties of the Glasses.

In each case, after melting for a period of 20 hours, the furnace was reduced in temperature to 1250°. This temperature was found to be suitable for the working of the first glasses melted at 1350°, and was maintained throughout both series of meltings so as to allow comparisons to be made in the working properties of the glasses, although, as was found later, it was by no means the best temperature at which to work some of the glasses. When this temperature had been attained and stabilised, the pots were opened for working, and in practically every case, but by far the more strongly marked in the glasses melted at 1400°, there was a viscous wavy layer on the surface of the glass. This layer was removed by skimming, but though this process improved the glass, it never removed all the waves and cords. There appeared to be no line of demarcation between this layer and the body of the glass, for the wavy layer seemed to be developed from, and be a modified form of the normal glass.

This view was supported by the fact that skimming improved the glass temporarily, but the surface fairly quickly became bad again, and in ordinary working out, the cordiness appeared to become worse as working proceeded, thus suggesting that the cordiness was due to the surface layer being colder than the body of the glass underneath it.

Another possibility was that the temperature at which the glass was being worked out was too low, and to test this point, the first half of the 100 lbs. melting of glass prepared from 100 per cent. cullet, was worked out at 1300°, with the result that the glass was practically free from cords. This temperature factor is further discussed in another report on the formation of cords.

The viscosities of these glasses, as judged by their ease of working, increased with the proportion of cullet in the batch, but this effect was far more marked in the glasses melted at 1400°

than in those melted at 1350°. It was much more difficult to work the 90 per cent. and 100 per cent. cullet glass melted at 1400°, than it was to work the corresponding glasses melted at 1350°. Just as the viscosity at a definite temperature varied in passing through the series, so the rate of change of viscosity increased as the proportion of cullet increased. This was particularly noticeable in glasses containing more than 50 per cent. of cullet and towards the end of the drawing operation, the setting of the glasses was accelerated.

In judging the viscosity and working range of these glasses from the drawing of rod and tube, it must be remembered, however, that they were all distinctly cordy, some more so than others, and as already mentioned, the cordiness varied in each melting depending on the time it had been worked since skimming. The apparent viscosity and the working range are very seriously affected by the amount of cord present. In fact, in some of the gatherings, the cords were so pronounced as to have a visible effect on the shape of the gatherings during marvering and to cause very uneven drawing into rod or tube. Such gatherings naturally appeared to have short working ranges. This point was also illustrated in the working of glass No. 780 (60 per cent. cullet, melted at 1400°), which was, perhaps, the least cordy of the glasses of this series, except that part of No. 783, which was worked out at 1300°, was one of the best glasses to draw into rod or tube.

In the glasses melted at 1400°, a further interesting feature was noticed. It has already been mentioned that as the glasses were worked out the cordiness increased, but in the glasses prepared at 1400°, it was noticed that this increase of cordiness was accompanied by the appearance or increasing occurrence of small solid particles, some of which, on examination under a high power microscope appeared to be crystalline. In the case of glass No. 780A (60 per cent. cullet in 50 lbs. pot), this process actually proceeded far enough for white opaque masses to be visible easily in the finished glasses and microscopic examination showed them to be separations of silica. This defect increased as the glass was being worked, thus indicating that the silica separation was proceeding during this time, and to prevent it

developing further the pot stopper was put up and the temperature raised about 50° for half an hour. At the end of this time, the glass had redissolved much of the previously separated silica.

Glass No. 780, the corresponding 60 per cent. cullet glass melted in the 100 lbs. pot, was practically free from this defect, thus suggesting that the particular composition or proportion of cullet was not the deciding factor in causing the silica separation from glass No. 780A, but that the temperature of working out was vitally important. It was partly to test this point that one half of glass No. 788 was worked out at 1300°, and in that case there were no signs of speckiness or of crystalline separations.

In order to ascertain if the composition of glass No. 781A which also showed definite signs of silica crystallisation, was not abnormal, its analysis was carried out along with the analysis of glass No. 770 which showed rather quick rate of refining. It was not considered necessary to analyse all the glasses systematically, but the results of such as were carried out are given in Table III.

The greatest deviations from the average composition are shown by glasses 768A and 773A. In neither of these cases, however, was any abnormal working feature found, a result which illustrates what we have previously found in the case of soda-lime glasses, namely, that whereas glasses of very similar composition may have viscosities and rates of setting distinctly different from one another, it is possible on the other hand to have appreciable differences of composition without producing marked changes in viscosity or setting rate.

TABLE III.

Glass No.	SiO_2	PbO	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	Total
768A ...	52·32	36·30	0·21	0·04	0·16	trace	0·04	10·32	99·89
770 ...	52·68	33·48	0·24	0·05	0·11	,,	0·04	13·14	99·74
771 ...	52·48	33·77	0·20	0·05	0·10	,,	0·04	13·38	100·02
773A ...	53·82	32·48	0·26	0·05	0·10	,,	0·04	13·14	99·89
776A ...	52·78	33·56	0·27	0·04	0·10	,,	0·04	13·18	99·97
779 ...	52·48	33·80	0·23	0·04	0·06	,,	0·04	13·28	99·93
781A ...	53·35	33·22	0·29	0·04	0·05	,,	0·04	13·08	100·07

General Conclusions.

The results of the study described in detail in this paper are very similar in general characteristics to those previously obtained with the soda-lime glasses. Increasing the proportion of cullet beyond 50 per cent. retards the rate of melting, although the retardation is not nearly so marked as with the soda-lime glass. The working properties of the resulting glasses also suffer a slight change as the proportion of cullet is increased in that the viscosity slightly increases, as does also the rate of setting. Although in our experiments these tests on the working properties were rendered a little difficult by the interfering action of cords, there was no doubt of the general increase of viscosity and rate of setting alluded to.

V. Experiments on the Re-melting of Glasses of Abnormal Working Properties.

A Report from the Department of Glass Technology, University of Sheffield, on investigations carried out on behalf of the Glass Research Association.

Abstract: Previous investigations have shown that the working properties of a soda-lime-silica glass differ according to the amount of moisture and the coarseness of the limestone particles in the batch. Further investigation has shown that whilst re-melting of glasses prepared from batch containing 5-15 per cent. moisture, or from limestone coarser than 30 mesh improved the homogeneity, the apparent viscosity was still greater. Re-melting with two parts of sodium sulphate (and 0·1 part of carbon) per 100 parts of glass, however, yielded glasses in every case as soft and easy working as the soda-lime-glass prepared from batch in the normal condition.

THE experiments which form the subject of this report arose out of our experiences in the preparation of soda-lime glasses from moist batches, and from a batch in which the limestone had been used in the form of rather coarse-grained particles, that is to say, coarser than 30 mesh.

The reports which embody these experiences have appeared in the Bulletin, the influence of water being discussed in Bulletin, 1923, No. 6, page 25, and the influence of grain size in Bulletin, 1924, No. 10, page 20.

It was shown in those reports that when the batch contained between 5 and 15 per cent. of moisture, the glass had a greater viscosity and a shorter working range than when made from comparatively dry batches, whilst the rate of melting and refining were also retarded with considerable amounts of moisture, and the resulting glass was liable to be cordy, stony, and lumpy, and in general, unsatisfactory.

This experience has been confirmed in a number of other investigations, and we have also found the viscosity enhanced and the working range slightly shortened, even in the case of potash-lead oxide glasses.

The use of the large-grained limestone in a soda-lime glass was also accompanied by a slowing up of the rate of melting and refining, producing a glass which was likely to be cordy and stony, whilst the viscosity and rate of setting were also somewhat greater than when using finely divided limestone.

Subsequent reports from us have dealt with the influence of cullet on the rate of melting and on the working properties of soda-lime glass, as also the influence of remelting cullet with small additions of the alkaline salts, namely, sodium carbonate, sodium nitrate, borax and sodium sulphate, the latter both with and without carbon. The influence of cullet was to enhance the viscosity, and to shorten the working range of the glass. No differences of chemical composition could be detected of such character as would explain these changes in viscosity.

The re-melting of cullet, however, with a small amount of an alkaline salt was shown to produce a glass as satisfactory from the working point of view as one prepared wholly from batch.

The question then arose as to whether the abnormal working properties exhibited by the soda-lime glasses prepared from wet batches or from coarse grained material would undergo any marked change if the glasses were re-melted either with or without a small amount of an alkaline salt.

A possible explanation of the abnormal properties might be want of homogeneity. The reduction of the glass, therefore, to small pieces followed by re-melting might be expected to remove the want of homogeneity, and if so, the question would arise as to whether the properties of the re-melted glass would resemble those of the batch-prepared glass, or the wholly cullet glass.

Experiments to test the above points were, therefore, conducted in three series, employing throughout a batch of the

following composition from which to prepare the glasses serving as raw material for the tests :

Sand	1000
Soda ash	325
Limestone	228

In the first and second series this batch was made up as in previous cases, with sand of 30 to 100 mesh grains, ordinary heavy soda ash, and finely divided limestone of about 200 mesh. Moisture was added to the extent of 10 per cent. in the first series, and 15 per cent. in the second.

In the third series Dowlow limestone was sieved, and the particles coarser than 30 mesh employed for the batch.

From each of these batches cullet was prepared, the melting operation being carried through to precisely the same stage as was reached in the previous investigations, in the course of which we had discovered the abnormal results, that is, the founding temperature was 1400°, and the period was 21 to 22 hours.

The resulting glass was rapidly chilled and broken up by ladling it into water, and the resulting dried cullet was then employed for further meltings, in one of which the cullet alone was re-melted, and in the other, two parts of sodium sulphate per 98 parts of cullet were added as well as a small quantity of carbon to the extent of 5 per cent. by weight of the sodium sulphate.

All the melting data, together with a statement of the compositions of the glasses, are given in Tables I., II. and III. appended. The general results may be expressed in a few words.

In the first place the meltings of the batch with 10 and 15 per cent. of moisture and with the coarse-grained limestone followed a course which confirmed in general our previous observations. A general improvement in the character of the two glasses melted from wet batches was obtained by the use, in the present investigation, of a pot of 100 lbs. capacity, whereas previously, pots of 28 or 56 lbs. capacity had been employed. The same characteristic increase of viscosity and shortened range of working were however, clearly marked as in previous observations.

When these glasses were re-melted from cullet alone, satisfactory homogeneous glasses were obtained in both cases, but the viscosity and rate of setting were still greater than in the case of the original glass, that is, still greater than when prepared from batch together with 10 or 15 per cent. of moisture. The slight increases of viscosity, in fact, made it desirable to work these re-melted glasses at a rather higher temperature, and it will be noted that whereas the batch-prepared glass was worked out at 1250°, we found it of advantage to use a temperature of 1300° in all cases for the re-melted glass to which no addition of saltcake had been made. This result appears to indicate, therefore, that the enhanced viscosity obtained by preparing glass from a wet batch, cannot be ascribed as due to lack of homogeneity in the glass; whilst, if the original glass owed its particular properties to the retention of moisture—a fact which yet has to be proved—the re-melted glass may also be supposed to contain no less an amount of water.

In general it will be found that the composition of the re-melted glass is not greatly different from the original.

The use of the small amount of sodium sulphate brought about satisfactory melting, and produced a glass not only less viscous and less quick-setting than the cullet-prepared glass, but also better than the original batch-prepared glass. This applies equally to the 15 as to the 10 per cent. moisture batch.

In reference to the glass prepared from coarse limestone, the melting made from the batch was scummy and stony. As previously found, it appeared, even making allowance for the unsatisfactory character of the melting, that the viscosity was somewhat greater than that of a glass prepared from fine limestone. The viscosity was, in fact, similar to that of the glass prepared from batch with 10 per cent. of moisture. This glass as a whole, without removal of the scum, was quenched in water, and the cullet, after being dried, was subjected to re-melting with, and without, sodium sulphate.

When melted alone, a glass was obtained free from any unmelted material, and in general, easier to work than the batch-prepared glass. At the same time the viscosity was not

TABLE I.

Glasses from Batch with 10 per cent. Moisture.

(*a*) *Melting Data.*

Melting Temperature : 1400°

Glass Ref. No.	Quantity Melted.	Materials Melted.	Time to Obtain Glass Batch-free.	Time to Obtain Glass Seed-free.	Working Temp.	Working Properties.
758, 758A, 758B	100 lb.	Batch + 10% moisture ...	4½-5 hrs.	10 hrs. ..	1250°	Good, clear glass, blue tint. No cordiness or wave, but distinctly viscous and rather quick setting. Otherwise satisfactory working properties.
762	„	Cullet alone, from glasses 758 & 758A	—	5-6 hrs.	1300°	Somewhat greater viscosity and slightly enhanced setting rate than in case of glass from the batch + 10% moisture.
766	„	98 parts of cullet from glasses 758 & 758A + 2 parts Na_2SO_4 + 0·1 part carbon.	—	5-6 hrs.	1250°	Sweeter, better-working, less viscous, and less quick-setting than either original or re-melted glass.

(*b*) *Glass Composition.*

Glass Ref. No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	Total.
758	75·55	0·30	0·08	9·84	trace	14·13	—	99·99
758A	75·77	0·56	0·08	9·86	„	13·74	—	100·01
762	75·40	0·52	0·10	9·85	„	13·06	—	99·92
766	75·48	0·66	0·10	9·54	„	14·34	0·10	100·12

TABLE II.

Glasses Melted from Batch with 15 per cent. Moisture.

(*a*) *Melting Data.*

Glass Ref. No.	Quantity Melted.	Materials Melted.	Time to Obtain Batch-free.	Time to Obtain Seed-free.	Working Temp.	Working Properties.
760 760A	100 lb.	Batch + 15% moisture...	5-5½ hrs.	13 hrs.	1250°	Easy working, without cords or waves. More viscous than glass from 10% moisture batch. Set distinctly quickly at end of tube drawing operation.
760B 760C 760D	56 lb.	Batch + 15% moisture " "	3½-4 hrs. "	10 hrs. 10-11 hrs.	1250° "	As above.
763	100 lb.	Cullet from 760 & 760A.	2-3 hrs.	5-6 hrs.	1300°	Clear, easy working glass, but more viscous and quick setting than the batch-prepared glass.
765	56 lb.	98 parts cullet from 760B & 760C and 2 parts Na_2SO_4 + 0·1 part carbon.	—	5½ hrs.	1300° 1270	Streaky because of much pot attack; but better working than glass from cullet only.

(*b*) *Glass Composition.*

Glass Ref. No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	Total.
760	76·34	0·67	0·06	9·31	trace	13·64	—	100·02
760A	76·07	0·61	0·06	9·43	"	13·85	—	100·02
763	75·78	0·59	0·08	9·62	"	13·90	—	99·97
765	75·42	0·99	0·12	9·27	"	14·07	0·12	99·99

TABLE III.

Glasses Melted from Limestone Coarser than 30 mesh.

(a) *Melting Data.*

Glass Ref. No.	Quantity Melted.	Materials Melted.	Time to Obtain Seed-free.	Time to Obtain Batch-free.	Working Temp.	Working Properties.
759	56 lb.	Batch with limestone coarser than 30 mesh	?	?	1250°	759. Scummy and stony because of some unmelted material.
759A	,,		?	?	,,	759A. Had little scum or stone. In both cases glass when free from stone was easy to work, although about as viscous as glass from 10 per cent. moisture batch. Bluish in tint.
759B	,,	Batch with limestone coarser than 30 mesh	?	?	,,	759B. Resembled 759.
759C	,,		?	?	,,	759C. Was very cordy and lumpy.
761	,,	Cullet from glasses 759 and 759A.	5*	8	1300°	No scum or unmelted material. Easier to work than 759 or 759A, but more viscous and quick setting.
764	,,	98 parts of cullet 759B and C., and two parts Na_2SO_4 + 0·1 part carbon.	2-3*	6	1250°	Clear, bright, easy-working glass. Less viscous and quick setting than original glass or remelted glass.

*Time required to remove the unmelted material remaining from melting of original glass.

(b) *Glass Composition.*

Glass Ref. No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	Total.
759B	70·07	0·65	0·07	9·44	trace	13·75	—	99·98
759C	70·20	0·60	0·08	9·67	,,	13·57	—	100·12
761	70·67	0·78	0·08	9·45	,,	13·12	—	100·10
764	75·42	0·85	0·12	9·44	,,	14·02	0·12	99·85

reduced, but was enhanced, and again there was a slight increase in the rate of setting. The temperature of working employed was 1300°.

Sodium sulphate produced an easy-working glass, less viscous and less quick setting than either the original or the remelted glass.

In all the results recorded, therefore, whatever the viscosity of the original melting, and whether produced by large moisture addition, or by coarse materials in the batch, the remelted glass was always slightly more viscous and quicker-setting. The use of sodium sulphate, on the other hand, in a small amount, led to a reduction of the viscosity and rate of setting, and in general, gave a very satisfactory glass.

VI. Some Observations on the Formation of Cords in Potash-Lead Oxide Glasses.

A Report from the Department of Glass Technology, University of Sheffield, on Investigations carried out on behalf of the Glass Research Association.

Abstract: Experiments have been made to ascertain, if possible, the cause of excessive cordiness and lumpiness in potash-lead oxide glasses. Such glasses were shown not to be prone to devitrification, and the addition of alumina to the batch and of artificial "pot runnings" did not produce lumpiness. The evidence suggests that temperature changes on opening a pot for working and the difficulty of ensuring homogeneity of the glass in the pot are likely causes of the defects.

DURING the many experimental meltings we have made, under widely varying conditions, we have been impressed with the difficulty of ensuring freedom from cords and waviness of glass produced from potash-red lead batches melted at temperatures of 1350° and 1400°. For the most part, the meltings of these glasses have been made by us entirely from batch, the mixture containing sand 900 parts, red lead 600, potash 300, potassium nitrate 48, and manganese dioxide 1. This batch has frequently been melted without addition of other substances, but in other cases potassium chloride, potassium sulphate, moisture in varying amounts, arsenious oxide and cullet have all been added for specific purposes.

The production of cords may be due to several reasons. One cause is probably the difference of density between the several components of a lead batch, favouring the segregation of the red lead, as the heaviest constituent, especially in dry batches. The slowness of diffusion in a glass retards the attainment of homogeneity. The addition of moisture to the

extent of 3–4 per cent. of the batch has been found by us to be beneficial in producing homogeneity, as will be understood by the above reference to segregation from dry batches.

A further cause of cordiness has usually been associated with pot attack. We ourselves have hitherto been inclined to regard this factor as important, especially in our own small scale experiments, because of the relatively larger pot surface per unit weight of glass than in commercial melting operations.

Some observations made, however, during experiments on the influence of cullet on the melting of lead glass, suggested that even as a contributory factor, pot attack as a cause of cordiness in lead glass must be held to be of distinctly less importance than our earlier impressions had warranted.

Concurrently with the observations just referred to, our attention was directed to two different types of cords which were causing defects at different glass works. Photographs were taken of the image of proofs (bulbs about 4-ins. diameter) thrown on a ground glass screen by a beam from a projection apparatus. Plate I. is a photograph showing the usual type of cord which, as indicated below, we believe to be associated with change of density due to surface cooling. Plate II. is of a type of cord, which we may describe as of the dot-and-dash pattern, a type we had not previously encountered. At a later stage in our work, however, we met with this type in drawing tubing from glass No. 757. Plates III. and IV. are magnifications, the first of the dot-and-dash cord shown in Plate II., and the second, of the example we found during our own experiments.

We were led, therefore, from the above observations, to carry out a series of experiments intended to throw light on the nature and cause of formation of the cords and the following pages record what was found.

The tests made were not the result of a completely thought out scheme of investigation, but suggested themselves to us from time to time as the work proceeded. It will be of advantage, however, first to describe the inhomogeneities noticed in some of the potash-lead oxide glasses melted previously by us.

I.

Description of the Cordiness and Lumpiness found in Potash-Lead Oxide Glasses.

During the meltings which were carried out to determine the effect of varying proportions of cullet on the melting and working properties of lead glasses it was noticed that every glass was cordy, some of them being very bad in this respect. As a rule, after skimming the glass, the gatherings at first were fairly free from cords, but got worse as working out proceeded. It was observed, however, in the case of one 100 lb. melting, which was only worked to within about six inches of the bottom of the pot and then allowed to cool down, that the lumps of glass broken from the mass, when cold, showed cordiness only extending for a depth of about 1½-in. from the surface downwards, the remaining 4-ins. being fairly free from cords. The photographs (Plates V. and VI.), are of such a lump of glass after slicing and polishing. Unfortunately, the block of glass was broken during the slicing. Plate V. shows the wavy character of the upper layer which received most chilling, whilst Plate VI. shows the streams of cooler glass sweeping downwards (right-hand side of photograph).

It was thus evident that the cords could scarcely be attributed to bad batch mixing or to uneven melting in such a case as this. It appeared that they were due to some circumstance attendant on the working of the glass, probably affecting the surface layer. One condition affecting the surface layer more than the body of the metal was clearly the fall of temperature on working. It was noticed that, generally speaking, the lower the working temperature, the more cordy the worked glass was likely to be, an observation in agreement with the fact that the cordiness generally got worse as the working out proceeded. Glass No. 783, melted from 100 per cent. cullet, when partly worked out at 1300° (interior of the pot temperature), was practically free from cords, while other glasses of the same series, worked out at 1250°, all showed cordiness in varying degrees.

It was also observed that the cordiness of each gathering appeared to get worse the longer the process of manipulating to

which it was subjected; this may have been because it was not easy to discern cords until the metal had cooled sufficiently to cause appreciable differences of viscosity in the separate portions comprising the gathering—supposing such separate portions to exist. Moreover, it was observed that slabs or discs cast from any one glass were less cordy than rod or tubing in the preparation for which the glass had undergone considerable manipulation outside the pot; and, further, the smaller drawings were less cordy than those from larger gatherings.

These observations alone made it exceedingly unlikely that the usual explanations offered for the existence of cords, namely, runnings from the sides of the pot and pot attack are correct. In fact, the pots used for these meltings suffered very little attack, and the corrosiveness of the batch seemed to bear no relationship to the cordiness or otherwise of the glass.

In a few of the meltings of the series referred to there were signs of devitrification, and in one glass, No. 780A, prepared with 60 per cent. of cullet in the batch, fairly large white lumps were formed which under the microscope were seen to be silica separations. In other glasses only small specks separated, but in every case the cords in the glass formed loops round the specks or lumps, thus confirming the conclusion that there were separations or devitrification. The photomicrograph, Plate VII., shows this cord formation radiating from tridymite crystals.

In some cases the specks were noticed in the midst of masses of tangled cords which caused the glass to draw out unevenly, giving rise to a series of lumps in the rod or tube which was being drawn. Small lumps appearing in the drawn glass were formed at places where the cords had been turned on themselves or had become bunched together. One piece of such lumpy glass is shown in Plate VIII.

After the foregoing observations had been made on glasses prepared from batch with varying proportions of cullet, similar phenomena were noted when melting the same type of lead glass from batch to which arsenious oxide, 10 parts per 1000

of sand, had been added. The glass developed a pronounced lumpiness during drawing operations. These clear glassy lumps always contained tangled cords; in some cases the cords seemed to be doubled back on themselves, while in others distinct sets of cords became mixed. Some of the lumps contained very small specks of solid material, which did not appear, however, to play any important part in the formation of the lump.

Two fairly large lumps were successfully isolated from tube drawn from glass No. 752/L/3. Under the microscope they were seen to be masses of tangled cords. They were crushed and the grains sieved between 10 and 30 mesh, and, after annealing, their density was determined at 25°, and found to be 3·1600. A portion of the same glass showing no lumpiness was similarly treated, and the density found to be 3·1853. This difference is very pronounced, being 2·5 units in the second place of decimals.

Analyses of the glasses were then made, when the following results were obtained.

	Lumpy Glass.		*Normal Glass.**
SiO_2	52·65	...	52·24
As_2O_3	0·62	...	0·67
Al_2O_3	0·40	...	0·26
Fe_2O_3	0·08	...	0·07
TiO_2	trace	...	trace
PbO	32·33	...	32·72
CaO	trace	...	trace
K_2O	13·88	...	13·82
	99·96	...	99·78

It is of interest to note that on calculating the density from the factors of W. L. Baillie (J. Soc. Chem. Ind. 1921, 40, 141), the density 3·206 was obtained from the normal glass, and 3·190 for the lumpy or abnormal glass.

*A carefully made check analysis gave
SiO_2 52·32%
Al_2O_3 0·31%

In this particular instance, lack of homogeneity could not arise through the failure of fused batch and cullet to diffuse completely since no cullet was added. Yet it is clear that segregation must either have occurred or been emphasised during the marvering and drawing operations. There is a perfectly definite difference in composition, in respect of the lead oxide and the silica, of the two different portions of the glass.

II.

The Possible Influence of Alumina in Causing Cords and Lumpiness in Potash-Lead Oxide Glasses.

We have already referred to the possibility of pot corrosion as the cause of cords, and although we have stated our evidence that this factor could scarcely be of real importance, it seemed wise to make a series of tests which would carry definite conviction.

The two portions of the arsenic-containing lead glasses, the normal and the lumpy, referred to in the preceding section contained distinctly differing amounts of alumina. At one time we were inclined to consider that the solubility of aluminium silicates in potash-lead oxide silicate glasses was possibly small and therefore produced layering and cords. It is true that we have examined electric light bulbs containing more than 1 per cent. of alumina and were unaware of any difficulty of obtaining lead glasses, with alumina, in a homogeneous state. The theory that alumina might be the one cause of the cords and lumps had to be regarded as untenable from the results of the following tests.

(1) *Tests with Alumina added to the Batch.*

Using the potash-lead oxide batch as stated on p. 75, for basis, amounts of calcined alumina were added so as to make the alumina content of the three separate glasses, 1, 3 and 5 per cent. respectively. These batches were melted in small crucibles for four hours at 1400° C., the glasses then poured on to the blowpipe after which they were marvered in the ordinary way and drawn into rod. The results were as follows :—

Melting No.	*Per cent.* Al_2O_3 *in Glass.*	*Remarks on Appearance of Rod.*
711	1	All Al_2O_3 dissolved giving clear glass with very few cords and no signs of lumps.
712	3	Gave stony glass, especially on surface; rod not excessively cordy; no lumps.
713	5	Very similar to No. 712.

(2) *Tests made by Pouring Alumina-containing Glass on to Surface of Potash-Lead Oxide Glass.*

Since alumina uniformly distributed among the batch did not cause lumpiness in the glass the effect of pouring one layer on another was tried. For this purpose, two small pot meltings were made, one of the normal potash lead oxide batch, and the other of glass No. 712 (*i.e.*, with 3 per cent. Al_2O_3). At the end of 3½ hours' melting at 1400°, the aluminous glass was skimmed, to remove as much undissolved Al_2O_3 as possible, and was then poured on to the top of the glass without alumina. The furnace was then kept at about 1350° for a further half-hour, after which the glass was gathered by pouring it from the pot on to the blowing iron, was marvered and drawn in the ordinary way. The rods contained a large number of small white specks of undissolved alumina; they were also somewhat cordy, but they were not lumpy.

Owing to the difficulty of gathering glass from small pots, in such a way as to get results comparable with those previously obtained on the larger scale, two further meltings in a 28 lb. covered pot were carried through and attempts were made to imitate excessive pot attack, causing pot runnings to flow on to the surface of the metal, by the following experiment.

The standard lead crystal batch (No. 752) was melted at 1400° and maintained at that temperature until perfectly free from stones and practically plain. In a small 1 lb. pot, a melting was made of a mixture of potash and 20 grams of finely ground

clay grog. After stirring up this mixture several times, and getting most of the grog into solution, it was poured on to the top of the glass in the 28 lb. pot, and allowed to remain there undisturbed for one hour, during which time the temperature was lowered to 1250°. On working the glass at this temperature the first gathering was very frothy, but in this respect the glass improved as it was worked down the pot. All the gatherings, however, especially the earlier ones, were stony and cordy, but not lumpy. The slabs which were poured from the glass in the bottom of the pot appeared distinctly better than the rod or tube previously drawn, both as regards seeds and cords. When cold, the rods and tubes drawn from the surface glass were very badly cracked owing to the non-homogeneity of the glass—but there were no signs of lumpiness in them, which may possibly be due to the fact that the glass poured on to the top of the melting, though containing alumina from the grog, was not more viscous than the normal glass.

To check this point, a small melting of glass, No. 713, with 5 per cent. alumina, was poured on to the top of an ordinary lead crystal glass (752). It was treated in exactly the same way as the previous one, but in working from first to last, the glass was stony and excessively cordy. There were, however, no clear glassy lumps such as it was hoped to produce.

The exact nature and cause of these lumps is, therefore, still undecided, but alumina does not appear as the prime cause.

III.

The Possibility of Incipient Devitrification as the Cause of Cordiness in Potash-Lead Oxide Glasses.

In experiments described in detail in another paper,* potash-lead oxide glasses were melted from a mixture of batch with 60 per cent. of cullet, in two pots, one containing 1 cwt., the other ½ cwt., of glass. On working out these glasses, it was found that the one from the ½ cwt. pot (Glass No. 780A), was cordy and also had undergone slight devitrification, whilst the

* This Bulletin pp. 55-56.

glass from the larger pot was very satisfactory. The question was raised as to the possibility of a mistake having been made in the composition of the batch and an analysis for silica content was made on each glass. The percentages of silica were found to be respectively 53·28 and 53·44 and the results proved that no error had occurred in batch mixing.

Slabs of the glass 780A, which showed devitrification, were examined under the microscope, and wherever a separation was found it was always surrounded by cords, and in some cases cords appeared to start as "tails" from the glassy material immediately surrounding the solid separation. (See Plate VII.).

In this connection it was found that on working out a glass which showed small crystallisation centres, a small gathering blown up till the glass was very thin, (less than 0·1 mm.), showed up the cords very plainly. In every case the small specks of solid material appeared to be the centres from which cords radiated in an irregular manner. Moreover every cord in the proof could be traced back to a solid particle. Plate IX. is a photomicrograph of a piece of thin walled glass showing the cords radiating from a centre of crystalline material.

We had only once previously had our attention directed to an example of devitrification occurring in glass at a tableware glass factory, but this type of glass has for so long been melted and worked in this country and elsewhere without difficulty, that a case of devitrification would only appear likely to arise from a cause of accidental character. Nevertheless, a series of tests was carried out to ascertain the degree of risk of devitrification in potash-lead oxide glasses of the type under study.

(1) *The Influence of Silica Content on Possible Devitrification.*

In the first of the tests, the object was to ascertain if, in the "crystal glass" of the approximate composition SiO_2 52-54, PbO 32-34, K_2O 11-13 per cent., the silica content was near the limit for devitrification. Accordingly, three meltings in small pots were made at 1400° from batches calculated to give 57 per cent, 60 per cent, and 63 per cent. of silica in the finished

glasses, the other constituents remaining in the same relative proportions to one another as in the standard glass.

Slabs were poured at a temperature of 1400° and the following observations made :—

Glass No.	*Calcd. percentage of* SiO_2 *present.*	*Observation.*
715	... 57 ...	A few very small specks of undissolved sand.
716	... 60 ...	Similar to 715.
717	... 63 ...	More small specks and a thin scum.

None of the slabs showed deposition of tridymite or other form of crystalline silica. There were no pronounced cords in any of them, but it must be remembered that rod or tube was not drawn.

(2) *Reheating Experiments with the View to Inducing Devitrification.*

(*a*) Experiments were first of all carried out on pieces of glass cut from wide tubing, the glasses investigated, namely, Nos. 779A, 780A, and 781A, all being very cordy. Glass No. 780A also contained evidence of tridymite crystallisation.

These samples were heated for a period of two hours each at a succession of temperatures, namely 700°, 750° and 800°, in an electric furnace without visible devitrification occurring in glasses 779A or 781A, or being extended in glass 780A.

(*b*) A melting from batch of the standard potash-lead oxide glass was made, the temperature was allowed to fall to 1300° after founding and refining, and 10 grams of tridymite scattered over the surface. At the end of this last operation the temperature had fallen to about 1250°, at which point it was maintained for 1½ hours.

On working out the glass at the end of this period it was found to be very " doggy," the rods and tubes being full of fine crystalline material. The glass gathered from the surface was naturally

worse than that from further down the pot, and it was noticed that during the working of each gathering the crystallisation appeared to get worse; however, as pointed out previously, this may have been due to the difficulty of seeing the separations at the gathering temperatures. That they were present when the gatherings were made was proved by taking a small gathering from low down the pot, and, without marvering of any kind, and with as short a delay as possible, it was blown up till the glass was very thin, in which condition it showed the presence of numerous small particles of crystalline material, each of which was the origin of a number of cordy strands radiating irregularly into the clear glass.

It was impossible to say from this experiment whether the tridymite had gone into solution to a small extent, or had caused any further crystallisation of silica from the glass; appearances were, if anything, in favour of the latter possibility.

(*c*) To try to determine this point precisely, two meltings (Nos. 718 and 719) were made in small pots at a temperature of 1350° - 1370°. At the end of three hours, the glass being quite free from batch and practically plain, the temperature was lowered to 1300°, and a single small particle of tridymite in a little moist filter paper was dropped on to the surface of the glass in each pot. During this operation the temperature fell to 1250°, where it was maintained for 2½ hours, and at the end of this period a slab was poured from one pot, and the other was allowed to cool down in situ.

No. 718 slab showed about half a dozen very minute specks of solid material. Three could be identified as clay, but the others could not be identified. In none of them was there any definite evidence of crystallisation such as was seen when tridymite was scattered on the surface of the 28 lb. melt.

The melt, No. 719, which was allowed to cool in the furnace, showed one small speck on the surface. It had the translucent appearance of unmelted silica and showed under the microscope the well-known crystalline fringe, but there was no sign of

this fringe having spread or grown into the glass. In neither of these meltings, therefore, could any evidence of the spreading of crystallisation after seeding be found.

(*d*) As a final test, another crucible was filled with the broken glass (782), remelted in an electric furnace at 1300°, and then cooled to 1250°. It was seeded with one small tridymite particle and the temperature maintained at 1250° for eight hours. There was no sign of crystallisation proceeding from the tridymite.

The test was repeated, on this occasion the temperature being held at 1150° for eight hours; but when cool, the tridymite particle could not be definitely identified. A few tiny specks could be seen on the surface, but none of them showed definite crystalline structure or fringes.

Conclusions.

The conclusions to be drawn from the above observations have not led us to a final solution of the cause of cordiness and lumpiness observed in potash-lead oxide glasses. The experiments made, however, show that solution of alumina from the fireclay of the pot cannot be regarded as a prime cause of the defect. The alteration of temperature as the pot is worked down, appears to produce marked cordiness through the chilling of the surface layer, and the setting up of convection currents. The ordinary cords of potash-lead oxide glasses may be due to this cause.

In this connection it would be of interest to investigate the alteration of density with temperature of the molten potash-lead oxide glasses. No change in the numerical value of such a physical property as density with change of temperature could account, however, for the existence of portions of different composition such as were found in the lumpy glass analysed.

Changes of composition might, indeed, result from devitrification. Our experiments, however, on this subject have not yet yielded any evidence sufficient to indicate that there is much danger or liability to devitrification in potash-lead oxide glasses of the type under investigation.

We might with advantage cite also the observations recorded by Le Chatelier (Compt. rend. 1916, 23, 40) on the enforced slow cooling, during German occupation, of the furnaces at Baccarat. Two types of glass had been melted at the time, the first, a potash-lead oxide glass made from a batch very similar in composition to our standard, with the addition of 1500 kg. of cullet per 600 kg. of batch; the second, a potash-soda-lead oxide of similar general composition with potash mainly replaced by soda. The mixture for the second glass was: Sand 300, soda ash 76, potash 14, red lead 200, potassium nitrate 4, arsenious oxide 4, cullet 2500.

Between August 24th and September 15th, the temperature of the pots had fallen to 800°, and the furnaces were then shut down. When cold, no sign of devitrification was found in the potash-lead oxide glass, although crystallisation had occurred in the soda-potash glass.

Changes of composition in the various parts of a pot of glass might arise from the process of "layering" of which one has heard frequently in glass works. Faraday (Phil. Trans., 1830), stated that during the course of his experiments on the preparation of optical glass he encountered big differences in density in the glass at the top and bottom of a pot only 6-in. deep. Thus, in different cases, he obtained as densities for the top and bottom layers, respectively, 3·38 and 4·04; 3·77 and 4·63; 3·81 and 4·75, and so on, for different glasses. The compositions of these separate layers were apparently not determined.

In our own investigations we have not tested for such differences of density with potash-lead oxide glasses, but any very appreciable differences would appear to be precluded by reason of the close agreement between the compositions of the various lead glass we have melted and analysed. The samples for analysis were not taken from any particular level in the pot and the general excellent agreement in composition does not warrant the view that chemical inhomogeneity existed to an extent in any way corresponding to such differences of density as Faraday observed.

As we have already shown that lumpiness consisted in the separation of two portions of glass of slightly differing composition and differing viscosity, we are still left without a definite clue as to whether separation on cooling occurred in an originally homogeneous glass, or a slightly inhomogeneous glass, indistinguishable as such at high temperature, became obviously so at a lower temperature owing to a magnification of viscosity differences.

Description of Photographs.

PLATE I. Photograph of proof of commercially produced potash-lead oxide glass showing usual type of cord. (×½)

PLATE II. Ditto, showing dot-and-dash type of cord. (×½)

PLATE III. Similar to Plate II. (×2)

PLATE IV. Magnification (×1½) of photograph of dot-and-dash cord found in tubing.

PLATE V. Photograph of block of glass (reduced to about one half of original size), showing wavy surface.

PLATE VI. Ditto showing also convection currents.

PLATE VII. Photomicrograph (×58), showing tridymite crystal devitrification and radiating cords.

PLATE VIII. Photograph of lumpy glass.

PLATE IX. Photomicrograph (×15) of piece of thin walled glass showing cords radiating from centre of crystallised material.

PLATE I

PLATE II.

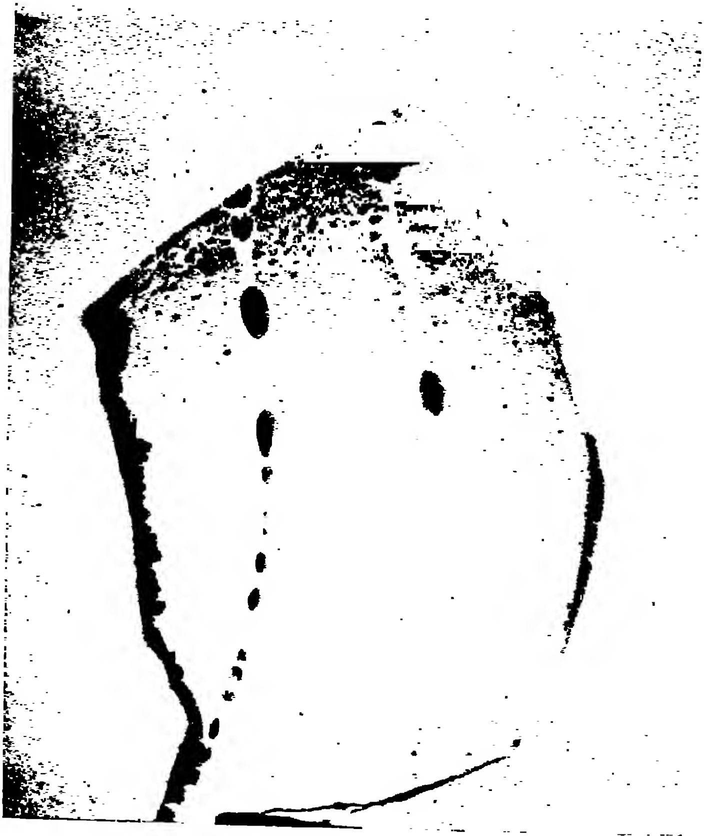

PLATE III.

PLATE IV.

PLATE V.

PLATE VI.

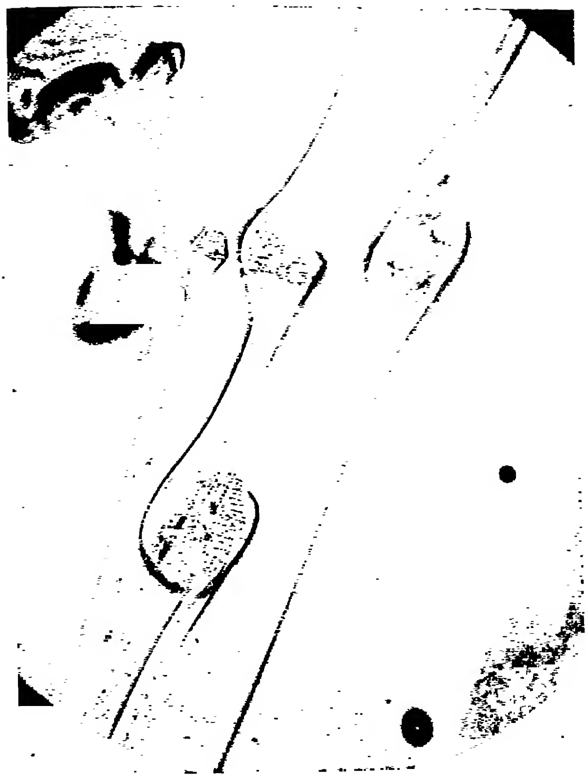

Plate VII.

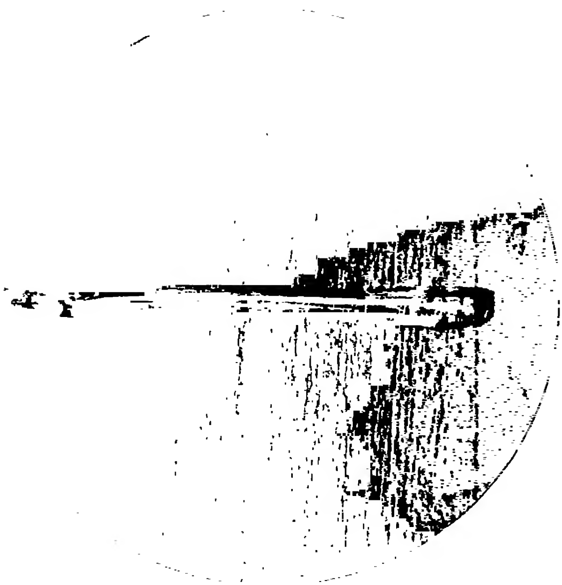

Plate VIII.

Plate IX.

VII. The Function of Arsenic in Glass.

Part V.—Potash-Lead Oxide Glasses.

A Report from the Department of Glass Technology, University of Sheffield, on investigations carried out on behalf of the Glass Research Association.

Abstract: Experiments have been made with a potash-lead oxide batch of the type used for tableware in this country, and with a potash-lead oxide bone ash opal glass. Amounts of arsenious oxide were added to the batch to produce the crystal glass varying from 2 to 50 parts per 1000 of sand, whilst in the batch for the opal glass 36 parts were present. Meltings were also made with varying amounts of moisture present up to about 4 per cent. It was found that throughout the series of glasses, from 78 per cent. to approximately 90 per cent. of the added arsenic was retained, from 80 to 90 per cent. of it approximately being left in the form of the higher oxide. In the potash-lead oxide glasses, increasing the proportion of arsenious oxide added accelerated the melting rate. The rate of refining was also increased up to a maximum, reached when between 20 and 30 parts were present in the batch. The batch with two parts of arsenious oxide produced the glass with best working properties. The most advantageous amount of moisture to be used when arsenious oxide is present was found to be between 1 and 2 per cent.

THE writer of "The Laboratory or School of Arts," a German work which was translated and published in this country in 1739, gives the following advice :—

"*To Make Glass Melting Easy.*

"Put into the melting Pot a little of Arsenick that has been fix'd with Nitre, this will make the glass mellow, and easy to fluviate."

The batches to which, from a study of the context, this piece of advice appears to apply are varied in composition, but all of them, by comparison with modern glasses, are very soft in character. One such batch consisted of silver sand 160 lbs., pot-ashes 60 lbs., crystalline arsenic 4 lbs., white lead 2 lbs., clear saltpetre 10 lbs., borax 2 lbs., a batch which is stated to give a beautiful crystal.

In previous reports on the special value of arsenic in glass-making we have seriously called into question whether the virtue of arsenic such as is suggested in the paragraph at the head of this paper has application to more modern glass batches, more especially those which do not contain sodium or potassium nitrate. In the case of the soda-lime glasses, we have definitely shown that between 75 and 100 per cent. of the arsenic added is usually retained in the glass in commercial meltings, and that even high temperature melting, and the presence of reducing agents do not very seriously diminish the amount of arsenic unless the reducing agent is present in very considerable excess. The rate of melting was not found to be assisted by the addition of arsenic, and in so far as the refining process was regarded as being dependent on the mechanical action of the arsenic escaping as vapour, the view that it assisted refining was untenable, because the arsenic remained in the glass.

These conclusions may or may not hold good in the case of the potash-lead oxide glasses, and the object of the investigation now recorded was to test this point.

For our purpose the batch which has served as the basis of study is the one we have described as standard potash-lead oxide batch as used in a series of other investigations. The composition is stated under A. As a variant on this glass we made two meltings of a potash-lead oxide bone ash opal, since in actual practice a considerably greater proportion of arsenious oxide is used in its preparation than is the case when melting the ordinary standard crystal glass. The batch for the opal glass is given under B.

A.

Sand	900
Red lead...	600
Potassium carbonate	300
Potassium nitrate	48
Manganese dioxide	1

B.

Sand	900
Red lead...	600
Potassium carbonate	300
Manganese dioxide	48
Bone ash	252
Arsenious oxide	36

A very large number of meltings, a complete list of which is given in Table I. appended, was made of the standard batch, to which increasing quantities of arsenious oxide were added, until ultimately as much as 50 parts of arsenic per 1000 of sand were present. Moreover, in order to ascertain if slight differences resulting from variation of moisture content of the batch (differences which are quite possible in commercial practice), would influence the retention of the arsenic, the meltings were in many cases carried out with the batch containing (1) less than

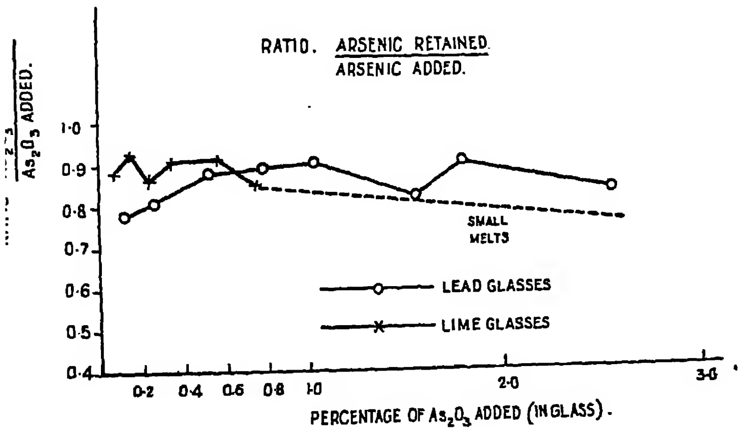

FIG. 1.

1 per cent. of moisture; (2) between 1 and 2 per cent. of moisture; and (3) with 4 per cent.

Analysis of the glasses showed that, just as with the soda-lime glasses, the bulk of the arsenic was retained. Fig. 1 shows the ratio of the arsenic retained to that added to the glass. In arriving at the value of this ratio we have taken the mean value for the arsenic found in all the glasses corresponding to a definite arsenic addition independently of the amount of moisture present. This means that the point in the diagram corresponding to the batch with two parts of arsenious oxide per 1000 of sand is the mean of no fewer than 20 glass analyses, and that corresponding to 10 parts, of 30 glass analyses.

It will be noted that throughout the range tested, with the exception of the first member for which the ratio is very slightly lower, more than 80 per cent. of the arsenic was retained. In general the ratio is maintained at a level between 80 and 90 per cent. For comparison purposes, the corresponding curve

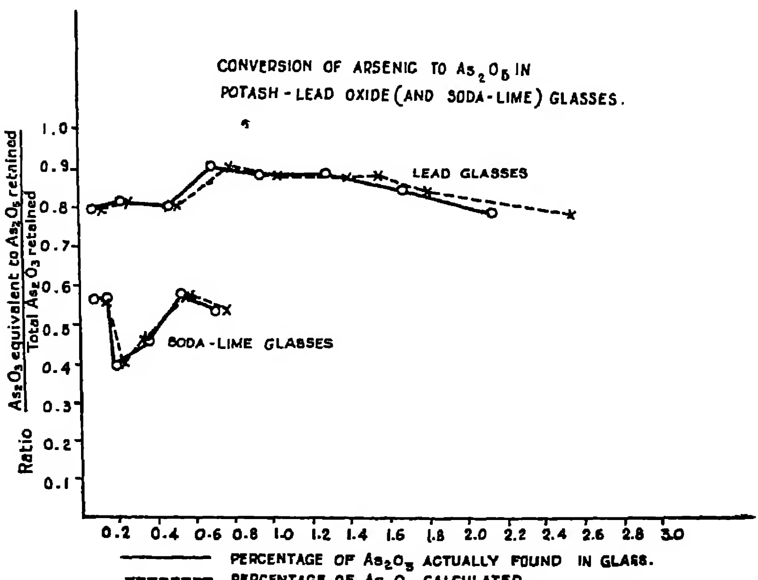

FIG. 2.

for the soda-lime glasses is added. The broken part of this latter curve relates to meltings done in small crucibles holding about 1 lb. of glass only.

Table II. sets out the compositions of the glasses in greater detail.

The greater part of the arsenic retained was found to be in the condition of the higher oxide. Fig. 2 shows the relationship between the amount of arsenic added to the batch, or retained in the glass, and the proportion of arsenic found in the state of higher oxidation. It will be seen that approximately the percentage of the arsenic oxide (As_2O_5) exceeds 80 per cent. of the total arsenic present. We might anticipate a greater proportion of the higher oxide in the lead than in the lime glasses (the corresponding curve for which is shown) on account of the strongly oxidising character of the lead glass batch.

It will be noted, by reference to Table II., that the general results apply to the opal glasses equally with the standard lead crystal glasses.

The Effect of Arsenic on the Rate of Melting and Refining of Lead Glasses.

Our results show a quite definite departure from those obtained with the soda-lime glasses, and there is no doubt that continuous addition of arsenic does speed up the rate of melting. Fig. 3 sets out in diagrammatic form the data which are given in greater detail in Table III. In Fig. 3 we have plotted the amount of arsenious oxide per 1000 of sand against the time in hours required for the melting of all trace of batch subsequent to the addition of the last charge. The curve clearly shows the downward trend in the number of hours needed.

We were inclined to think that a minimum point in the melting rate might be reached, especially since in the glasses with 50 parts of arsenic per 1000 of sand in the batch there was an increasing tendency for the formation of scum which remained until the close of the founding period. Up to the addition of 50 parts of arsenious oxide, however, no minimum

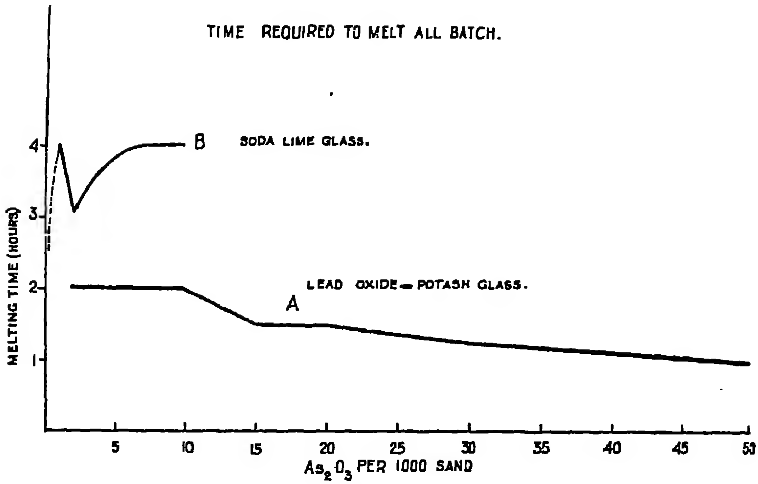

FIG. 3.

was discovered, and it did not appear of value to proceed beyond this point.

The rate of refining, however, did appear to reach a maximum. This is indicated in Fig. 4, and it will be seen that the best results were obtained with between 20 and 30 parts of arsenious oxide per 1000 of sand.

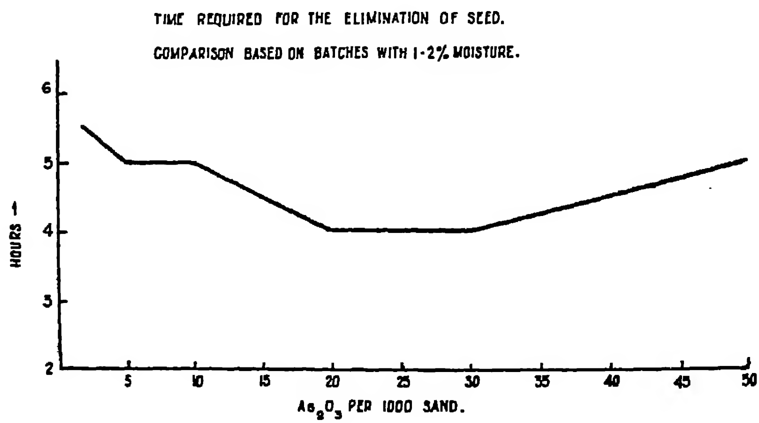

FIG. 4.

The Influence of Arsenious Oxide on the Working Properties of the Glass.

The glass prepared from the batch containing only two parts of arsenious oxide per 1000 of sand was an excellent glass for working, and there appeared to be no essential difference whether the batch contained 1 per cent. or 4 per cent. of moisture. With five parts of arsenious oxide in the batch the resulting glass was in all cases less satisfactory. Even when to start with, working was easy, the glass subsequently became cordy and ragged. Ten parts of arsenious oxide gave a glass still less satisfactory.

Fifteen and 30 parts of arsenious oxide, however, produced glasses which were rather more favourable to working operations than did those with 5 and 10 parts. The maximum amount of arsenious oxide, namely, 50 parts, however, produced a very poor glass from the point of view of working.

We found at a later stage that the temperature of 1250° which had been adopted as the general standard temperature for the working of the glasses, was not so satisfactory as 1300°; thus glasses 752.G/3, G/4, H/3, H/4, which were worked out at 1300°, could under this condition be manipulated more easily, and gave little trouble due to cordiness. Attention is directed in another paper, namely, that entitled Some Observations on the Production of Cords in Potash-Lead Oxide Glasses* to this advantage of working at 1300° instead of 1250°.

Notes on the working properties of each glass are given in Table V.

The Influence of Moisture in Combination with Arsenic.

As already stated, some of the batches melted were prepared from well-dried materials, so that the batch contained less than 1 per cent. of moisture. The actual

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* This Bulletin, pp. 75-88.

amount of moisture present in the so-called "dry" batches was in the neighbourhood of 0·8 per cent. Other batches, indeed, the majority, contained between 1 and 2 per cent. A few contained 4 per cent., water being added to produce this total.

There was a definite object in making those experiment with varying amounts of moisture. The so-called "dry" batches were employed so that we could determine the influence of arsenic without complication with the effect of moisture. The batches with 4 per cent. were tested because this particular percentage had, as the result of an earlier investigation, been shown to exert the most favourable influence on the rate of melting and refining in the absence of arsenic.

So far as the retention of arsenic in the glass is concerned, no difference could be determined according as the batch was dry or had 4 per cent. of moisture present. The melting and refining rates were, however, influenced quite definitely when only 2 or 5 parts of arsenious oxide were present. Reference to Table IV. will show quite clearly that the batches which were both slowest in melting and in becoming seed free were those which were dry.

Those containing 4 per cent. were less advantageous than those with 1-2 per cent. moisture. It appears, therefore, when arsenious oxide is present in a potash-lead oxide batch to an extent not greater than five parts per 1000 of sand, that the most favourable results are obtained when the batch contains between 1 and 2 per cent. of moisture.

When 10 or more than 10 parts of arsenious oxide were present the variation of the moisture content within the limits tested did not appear to produce any variation in the rate of melting or refining.

With reference to the influence on the working properties, the only noticeable feature was that the glasses prepared from the batch containing 4 per cent. of moisture were more viscous than the others containing less moisture.

TABLE I.—List of Meltings of Potash-Lead Oxide Glasses containing Arsenic.

A. *Standard English Crystal Glass.*

Glass Ref. No.	Capacity of Pot.	As_2O_3 per 1000lb. Sand.	Calcd. Percentage of As_2O_3 in Glass.	Moisture Content of Batch.
740.A	100 ,,	2	0·11	
740.A/2	56 ,,	2	0·11	—
752.A	100 ,,	2	0·11	"dry"
752.A/2	56 ,,	2	0·11	"dry"
752.B	100 ,,	2	0·11	4 per cent.
752.B/2	56 ,,	2	0·11	4 per cent.
752.B/3	100 ,,	2	0·11	4 per cent.
752.B/4	56 ,,	2	0·11	4 per cent.
752.E	100 ,,	2	0·11	1-2 per cent.
752.E/2	56 ,,	2	0·11	1-2 per cent.
740.B	100 ,,	5	0·26	—
740.B/2	56 ,,	5	0·26	—
752.C	100 ,,	5	0·26	"dry"
752.C/2	56 ,,	5	0·26	"dry"
752.D	100 ,,	5	0·26	4 per cent.
752.D/2	56 ,,	5	0·26	4 per cent.
752.D/4	56 ,,	5	0·26	4 per cent.
752.F	100 ,,	5	0·26	1-2 per cent.
752.F/2	56 ,,	5	0·26	1-2 per cent.
752.G	100 ,,	10	0·52	"dry" 0·85
752.G/2	56 ,,	10	0·52	"dry" 0·84
752.G/3	100 ,,	10	0·52	"dry"
752.G/4	56 ,,	10	0·52	"dry"
752.H	100 ,,	10	0·52	1-2 per cent. 1·90
752.H/2	56 ,,	10	0·52	1·79
752.H/3	100 ,,	10	0·52	1-2 per cent.
752.H/4	56 ,,	10	0·52	1-2 per cent.
752.J	100 ,,	10	0·52	4 per cent. 4·34
752.J/2	56 ,,	10	0·52	4·35
752.J/3	100 ,,	10	0·52	4 per cent.
752.J/4	56 ,,	10	0·52	4 per cent.
752.K	100 ,,	10	0·52	1·73
752.K/2	56 ,,	10	0·52	1·77
752.P	100 ,,	10	0·52	4·35
740.C	100 ,,	11·1	0·58	—
740.C/2	56 ,,	11·1	0·58	—
752.L	100 ,,	15	0·78	1·78
752.L/2	56 ,,	15	0·78	1·79
752.L/3	100 ,,	15	0·78	1-2 per cent.
752.L/4	56 ,,	15	0·78	1-2 per cent.
752.M	100 ,,	20	1·04	1·75
752.M/2	56 ,,	20	1·04	1·84
752.N	100 ,,	30	1·55	1·82
752.N/2	56 ,,	30	1·55	1·80
752.Q	100 ,,	50	2·56	—
752.Q/2	56 ,,	50	2·56	—

B. *Potash-Lead Oxide Bone Ash Opal Glass.*

Glass Ref. No.	Capacity of Pot.	As_2O_3 per 1000lb. Sand.	Calcd. Percentage of As_2O_3 in Glass.	Moisture Content of Batch.
752.R	100 lbs.	40	1·80	—
752.R/2	56 ,,	40	1·80	—

TABLE II.

Composition of the Glasses Melted.

A. *Potash-Lead Oxide Crystal Glasses.*

	SiO_2	PbO	As_2O_3	As_2O_5	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Total.	Total As as As_2O_3	Calcd. Total As_2O_3
740.A	53·81	32·27	0·02	0·07	0·26	0·02	0·06	0·08	trace	13·18	99·77	0·08	0·11
740.A/2	52·75	33·31	trace	0·07	0·23	0·03	0·04	0·07	,,	13·60	100·10	0·07	0·11
752.A	53·13	33·00	0·05	0·04	0·36	0·03	0·03	trace	trace	13·27	99·91	0·08	0·11
752.A/2	55·12	31·49	0·02	0·06	0·23	0·04	0·04	trace	trace	13·15	100·15	0·07	0·11
752.B	53·66	32·72	0·01	0·07	0·22	0·03	0·05	trace	trace	13·35	100·11	0·07	0·11
752.B/2	52·55	33·60	0·03	0·06	0·30	0·03	0·04	trace	trace	13·21	99·82	0·08	0·11
752.B/3	52·78	33·14	0·02	0·09	0·18	0·03	0·04	trace	trace	13·48	99·76	0·10	0·11
752.B/4	51·04	35·27	0·02	0·12	0·53	0·03	0·05	trace	trace	12·76	99·82	0·14	0·11
752.E	52·92	33·23	0·02	0·08	0·15	0·03	0·04	trace	trace	13·34	99·81	0·09	0·11
752.E/2	51·89	34·30	0·03	0·08	0·24	0·04	0·04	trace	trace	13·26	99·86	0·10	0·11
740.B	52·55	33·02	0·04	0·20	0·21	0·03	0·05	0·14	trace	13·66	99·90	0·21	0·26
740.B/2	54·03	31·67	0·05	0·16	0·17	0·03	0·04	0·05	trace	13·04	99·84	0·19	0·26
752.C	53·30	32·78	0·05	0·17	0·21	0·03	0·04	trace	trace	13·47	100·05	0·20	0·26
752.C/2	53·78	32·56	0·05	0·19	0·36	0·03	0·04	trace	trace	13·08	100·09	0·22	0·26
752.D	53·78	32·76	0·04	0·19	0·29	0·02	0·04	trace	trace	13·04	100·16	0·20	0·26
752.D/2	53·67	32·89	0·05	0·20	0·22	0·03	0·04	trace	trace	13·03	100·13	0·22	0·26
752.D/4	51·27	34·80	0·04	0·18	0·46	0·03	0·05	trace	trace	13·19	100·02	0·19	0·26
752.F	52·71	33·17	0·05	0·21	0·31	0·03	0·04	trace	trace	13·38	99·90	0·23	0·26
752.F/2	51·84	34·14	0·04	0·20	0·16	0·04	0·05	trace	trace	13·38	99·85	0·22	0·26
752.G	52·67	33·62	0·05	0·44	0·34	0·03	0·05	trace	trace	12·73	99·93	0·43	0·52
752.G/2	—	—	0·04	0·38	—	—	—	—	—	—	—	0·39	0·52
752.G/3	—	—	0·08	0·45	—	—	—	—	—	—	—	0·47	0·52
752.G/4	—	—	0·11	0·41	—	—	—	—	—	—	—	0·46	0·52

TABLE II. (continued).

	SiO_2	PbO	As_2O_3	As_2O_5	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Total.	Total As as As_2O_3	Calcd. Total As_2O_3
752.H	—	—	0·09	0·35	—	—	—	—	—	—	—	0·40	0·52
752.H/3	—	—	0·07	0·48	—	—	—	—	—	—	—	0·48	0·52
752.H/4	—	—	0·07	0·44	—	—	—	—	—	—	—	0·46	0·52
752.J	53·23	32·94	0·14	0·42	0·27	0·02	0·05	trace	trace	12·02	99·99	0·44	0·52
752.J/2	—	—	0·06	0·25	—	—	—	—	—	—	—	0·29	0·52
752.J/3	—	—	0·04	0·51	—	—	—	—	—	—	—	0·48	0·52
752.J/4	—	—	0·07	0·44	—	—	—	—	—	—	—	0·40	0·52
752.K	—	—	0·09	0·40	—	—	—	—	—	—	—	0·44	0·52
752.K/2	—	—	0·11	0·40	—	—	—	—	—	—	—	0·46	0·52
752.P	51·42	33·27	0·07	0·56	0·38	0·04	0·04	trace	trace	14·14	99·92	0·56	0·52
740.C	53·63	31·63	0·06	0·44	0·35	0·04	0·05	0·11	trace	13·66	99·97	0·44	0·52
740.C/2	54·56	31·66	0·11	0·40	0·29	0·03	0·04	0·06	trace	12·80	100·01	0·47	0·52
752.L	53·39	34·11	0·14	0·60	0·25	0·04	0·04	trace	trace	11·41	99·98	0·66	0·78
752.L/2	—	—	0·06	0·84	—	—	—	—	—	—	—	0·79	0·78
752.L/3	—	—	0·06	0·74	—	—	—	—	—	—	—	0·70	0·78
752.L/4	—	—	0·09	0·63	—	—	—	—	—	—	—	0·63	0·78
752.M	—	—	0·10	0·92	—	—	—	—	—	—	—	0.90	1·04
752.M/2	—	—	0·12	1·01	—	—	—	—	—	—	—	0·98	1·04
752.N	51·22	32·56	0·10	1·41	0·44	0·03	0·04	trace	trace	14·08	99·88	1·32	1·55
752.N/2	—	—	0·19	1·19	—	—	—	—	—	—	—	1·22	1·55
752.Q	—	—	0·50	1·82	—	—	—	—	—	—	—	2·07	2·56
752.Q/2	—	—	0·45	2·14	—	—	—	—	—	—	—	2·20	2·56
B. *Arsenic Content of Bone Ash Opal Glasses.*													
752.R	—	—	0·27	1·18	—	—	—	—	—	—	—	1·64	1·80
752.R/2	—	—	0·24	1·30	—	—	—	—	—	—	—	1·74	1·80

TABLE III.—Relationship between Concentration of Arsenic in the Batch and
(1) The Ratio of Arsenic retained to Arsenic added.
(2) The Ratio of Arsenic retained as As_2O_5 to Total Arsenic.

Glass Ref No.	Parts of As_2O_3 in Batch per 1000 Sand.	Ratio:— As_2O_3 retained: As_2O_3 added.	Ratio:— As_2O_3 equivalent to As_2O_5 retained: Total As_2O_3 retained.
740.A	2	0·73	0·86
740.A/2	2	0·64	1·00
752.A	2	0·77	0·41
752.A/2	2	0·59	0·77
752.B	2	0·64	0·86
752.B/2	2	0·62	0·60
752.B/3	2	0·91	0·80
752.B/4	2	1·02	0·85
752.E	2	0·77	0·82
752.E/2	2	0·86	0·79
740.B	5	0·81	0·81
740.B/2	5	0·73	0·74
752.C	5	0·75	0·77
752.C/2	5	0·85	0·77
752.D	5	0·79	0·87
752.D/2	5	0·87	0·79
752.D/4	5	0·71	0·78
752.F	5	0·86	0·80
752.F/2	5	0·84	0·84
752.G	10	0·83	0·88
752.G/2	10	0·74	0·81
752/.G3	10	0·90	0·82
752.G/4	10	0·87	0·77
752.H	10	0·75	0·79
752.H/3	10	0·92	0·86
752.H/4	10	0·88	0·85
752.J	10	0·85	0·69
752.J/2	10	0.51	0·79
752.J/3	10	0·91	0·91
752.J/4	10	0·87	0·85
752.K	10	0·85	0·80
752.K/2	10	0·88	0·77
740.C	11·1	0·77	0·85
740.C/2	11·1	0·80	0·76
752.L	15	0·84	0·79
752.L/2	15	1·06	0·92
752.L/3	15	0·90	0·91
752.L/4	15	0·81	0·86
752.M	20	0·86	0·89
752.M/2	20	0·94	0·88
752.N	30	0·85	0·93
752.N/2	30	0·79	0·84
752.Q	50	0·81	0·76
752.Q/2	50	0·86	0·79
752.R	40	0.91	0·83
752.R/2	40	0·96	0·86

TABLE IV.

Relationship between Arsenic Content of Batch and Time Required for Batch Melting and for Elimination of Seed.

Glass No.	Moisture Content.	As_2O_3 per 1000 Sand.	Time in hours from last filling till batch free.	Time in hours from last filling till seed free.
752.A	dry	2	3	8
„ A/2	dry	2	3	8
„ B	4%	2	2½	6
„ B/2	4%	2	2½	6
„ B/3	4%	2	2½	6½
„ B/4	4%	2	2	—
„ E	1-2%	2	2	5½
„ E/2	1-2%	2	2	5½
„ C	dry	5	2½	8
„ C/2	dry	5	2½	7½
„ D	4%	5	2½	6
„ D/2	4%	5	2½	6
„ D/4	4%	5	2½	5½
„ F	1-2%	5	2	5
„ F/2	1-2%	5	2	5
„ G	dry	10	2	5
„ G/2	dry	10	2	4½
„ G/3	dry	10	2	5
„ G/4	dry	10	2	5
„ H	1-2%	10	2	4½
„ H/2	1-2%	10	2	5
„ H/3	1-2%	10	2	5
„ H/4	1-2%	10	2	5
„ J	4%	10	2	5
„ J/2	4%	10	2	4½
„ J/3*	4%	10	—	—
„ J/4	4%	10	2	4½
„ K	1-2%	10	2	5
„ K/2	1-2%	10	2	4½
„ P‡	4%	10	1½	5
„ L	1-2%	15	1½	4½
„ L/2	1-2%	15	1½	4½
„ L/3	1-2%	15	2	5
„ L/4	1-2%	15	1	4
„ M	1-2%	20	1½	4
„ M/2	1-2%	20	1½	3
„ N	1-2%	30	1½	4
„ N/2	1-2%	30	1	3
„ Q	1-2%	50	1	5
„ Q/2	1-2%	50	1	4

* Large blower broke down after one hour melting, and small one was used till repairs were completed.

‡ Melted at 1450°

TABLE V.

The Working Properties of the Potash-Lead Oxide Glasses containing Arsenic.

Glass No.	Pot Capacity.	As_2O_3 per 1000 Sand.	Moisture Content.	Working Properties.
752.A	100 lbs.	2	dry	Soft. Easy working.
„ A/2	56 „	2	dry	Soft.
„ E	100 „	2	1-2%	Easy working; drew well into rod and tube.
„ E/2	56 „	2	1-2%	
„ B	100 „	2	4%	
„ B/2	56 „	2	4%	Easy working.
„ B/3	100 „	2	4%	
„ B/4	56 „	2	4%	Very wavy and ragged; not like B, B/2 & B/3.
„ C	100 „	5	dry	Good at first; quickly became ragged.
„ C/2	56 „	5	dry	Ragged, cordy, doggy, and brittle.
„ D	100 „	5	4%	More viscous than " C " glasses.
„ D/2	56 „	5	4%	Cordy, doggy & viscous.
„ D/4	56 „	5	4%	Good until it developed lumpiness.
„ F	100 „	5	1-2%	Not quite so easy to work as " E " glasses.
„ F/2	56 „	5	1-2%	
„ G	100 „	10	dry	Stony, lumpy & wavy; not good working metal.
„ G/2	56 „	10	dry	
„ G/3	100 „	10	dry	At higher temperature (1300°) gave fairly easy working and drawing; some little cord.
„ G/4	56 „	10	dry	
„ H	100 „	10	1-2%	Good and easy working, but developed cords.
„ H/2	56 „	10	1-2%	Cordy and lumpy.
„ H/3	100 „	10	1-2%	At higher temperature (1300°) was fairly soft and easy working.
„ H/4	56 „	10	1-2%	

TABLE V. (Continued).

Glass No.	Pot Capacity.	As_2O_3 per 1000 Sand.	Moisture Content.	Working Properties.
„ J	100 „	10	4%	More viscous than "H" glasses.
„ J/2	56 „	10	4%	Similar to "J," but more wavy.
„ J/3	100 „	10	4%	Doggy and ragged when drawn.
„ J/4	56 „	10	4%	Rather more viscous than H/4, and shorter working range.
„ K	100 „	10	1-2%	Stony, wavy, poor working metal.
„ K/2	56 „	10	1-2%	
„ P	100 „	10	1-2%	Stony and wavy; not easy working.
„ L	100 „	15	1-2%	Easier working than "J" or "K"; some stone and cord, rather soft to gather.
„ L/2	56 „	15	1-2%	
„ L/3	—	—	—	
„ L/4	100 „	15	1-2%	Not good working metal.
„ M	56 „	20	1-2%	Stony and cordy; not easy to work.
„ N	100 „	30	1-2%	Fairly easy to work after heavy scum had been removed.
„ N/2	56 „	30	1-2%	
„ Q	56 „	50	1-2%	Very bad at first; appeared devitrified. Improvement as pot was worked, but never good.
„ Q/2	56 „	50	1-2%	

VIII. A Note on the Conversion of Arsenious to Arsenic Oxide during the Glass Melting Process.

A Report from the Department of Glass Technology on investigations carried out on behalf of the Glass Research Association.

A SERIES of reports presented by us to the Glass Research Association have shown that not only is most of the arsenic added to batches for soda-lime and potash-lead oxide glasses retained in the product, but further, the proportion of the residual arsenic in the arsenic state is greater than that in the arsenious state in which the arsenic was introduced.

Clearly, combination with oxygen must occur during the melting process, and the question as to where this source of oxygen is obtained is of very considerable interest. It is obvious in the case of the potash-lead oxide glasses that oxidation could occur through the agency of the red lead and potassium nitrate employed, but there is no clear explanation, however, of the source of oxygen in the soda-lime glass melted without the presence of oxidising agents. The air imprisoned in the batch seems the only possible source.

A series of experiments showed that no appreciable oxidation of the arsenic occurred during the analysis of the glasses. In this connection a test was made in which the conditions of analysis were varied. The sample of glass used for the purpose contained 0·63 per cent. of total arsenic calculated as As_2O_3 and 1 gm. of it finely powdered, was evaporated with 1 to 2 cc. of H_2SO_4 (1 : 1) and 20 cc. HF in a platinum dish or large crucible. In the set of experiments tried, pairs of tests were worked as follows :—

(*a*) The glass was fumed down with the acids fairly rapidly, namely, within the period of one hour.

(*b*) The fuming down was done slowly, taking at least six hours, and halfway through the process the dish was allowed to stand in contact with air all night.

(*c*) To the fuming liquid was first added 25 cc. of fully aerated water, after which evaporation was slowly carried out.

Arsenic present as As_2O_5 was determined, the results being as follows :—

Method.	*Per cent.* As_2O_5.
Rapid fuming (1)	0·48
(2)	0·49
Very slow fuming (1)	0·50
(2)	0·48
Addition of aerated water (1)	0·49
(2)	0·50

It is evident from the results that no appreciable oxidation could have occurred during the process of breaking down the glass.

An experiment was now carried out in which a soda-lime batch, containing 10 gm. of sand, 3·25 gm. of soda-ash, 2·28 gm. limespar, and 0·10 gm. arsenious oxide, was heated in an atmosphere of nitrogen in a fireclay boat in an electric tube furnace.

A stream of nitrogen prepared from ammonium nitrite and washed, in two separate bottles, by alkaline pyrogallol solution, was passed through the tube to sweep out the air thoroughly before raising the temperature. The heating and subsequent cooling were also conducted in an atmosphere of nitrogen, except that the stream of the latter was cut down during the period when the batch itself was evolving gas.

The temperature was recorded by a thermocouple, the junction of which was adjacent to the fireclay boat.

Evolution of carbon dioxide was first noted in appreciable quantity at about 680° and continued briskly until about 780° at which point it stopped and was no longer observed.

It was the intention to raise the temperature to 1400°, the normal founding temperature adopted by us in glass melting, but at 1150°, unfortunately, the porcelain tube containing the boat became distinctly swollen and burst the heating coil. The current was then cut off and the tube allowed to cool. It was found necessary to break the tube in order to remove the boat, and when this had been done a clear layer of glass was found in the latter together with an upper opaque layer, probably highly siliceous. The two layers were carefully separated and about 3½ gm. of the clear layer and 5½ gm. of the opaque layer obtained.

On estimation the arsenic contents of the two layers were found to be :—

	Total Arsenic as As_2O_3	Arsenic as As_2O_5
Clear layer	0·64 ...	0·62
Opaque layer	0·48 ...	0·41

The extensiveness of conversion of the arsenious oxide to the arsenic condition is astonishing. It is proportionately greater than was found when the batch was melted in bulk in a pot heated by a gas-fired furnace. Although we would wish to be able to confirm the experiment by repetition, it scarcely appears that the air content of the batch can, as suggested, provide the necessary supply of oxygen for oxidation.

In respect of the arsenic present in the 9 grams of glass recovered, 4·3 cc. of oxygen, equivalent to 20 cc. of air, would have been needed for oxidation. As the tube was well swept out with nitrogen before heat was applied, it does not seem conceivable that air could have supplied the source of oxygen.

The results of the above observations make the problem, as to the source of oxygen, of still greater interest. It is conceivable that the arsenious oxide is a more powerful reducing agent than has formerly been supposed, and may even reduce the sodium carbonate present in the batch with the

liberation of carbon monoxide; or again, the arsenious oxide itself might be decomposed according to the equation:

$$5\ As_2O_3 = 3\ As_2O_5 + 4\ As.$$

Such a change, however, would involve a much greater proportional loss of arsenic than we have found in our investigations.

We propose, as soon as can conveniently be done, to carry out further experiments to discover the source of oxygen which brings about the conversion.

IX. Notes on certain Phases of the Work of the Association.

By the Director of Research.

Synopsis.

IMPERFECTIONS : STONES : (*a*) *Batch Stones*, (*b*) *Clay Stones* ; DEVITRIFICATION ; CRYSTALLISATION ; SALTS ; SLACKS ; DIM ; BLOOM ; CLOUDING ; SMUDGING ; SEEDS AND BLISTERS : *Air Seeds*, *Reboil Seeds*, *Batch Seeds* ; CORDS ; CHECKS AND CRIZZLES. — PIPES — ANNEALING — ACID POLISHING — BADGING — LIME — ELECTRICAL CONDUCTIVITY — REFRACTORIES.

IMPERFECTIONS.

BEFORE discussing the imperfections which have been dealt with from time to time at the request of Members, I wish to refer to methods and apparatus used in investigating the character and cause of such imperfections. The microscope is probably the most useful and accurate instrument that can be employed, and I now greatly deplore the fact that we did not utilise more time and money in developing the binocular microscope and its use in investigating the characters and causes of these imperfections.

In January, 1923, I issued a pamphlet (No. 4) under the caption " Use of the Microscope as an Instrument of Control." and therein I set forth the advantages of the binocular microscope over the monocular type, and the procedure to be followed in the examination of sands and raw materials whereby a determination of their purity could be obtained sufficiently accurate to permit of acceptance or rejection. I have used the microscope for the past twenty years as the primary and most accurate means of investigating imperfections, and I am convinced that the binocular type has many advantages and could be so developed

as to be a very useful instrument, but, as above suggested, there were so many researches in hand, and so many calls upon our time in carrying out industrial research, that it was impossible for us to develop the polarising binocular microscope and its application to a degree approaching perfection. However, the instrument which was developed through the efforts of my assistant, Mr. R. E. Leeds, was sufficiently perfected to enable one skilled in its use to determine accurately and positively the characteristics and, in many instances, the causes of the various imperfections, and I will endeavour to set forth the procedure followed. Imperfections may be classed as under :—

Stones	Bloom
Seeds and Blisters	Clouding
Devitrification	Smudging
Salts	Cords
Slacks	Checks
Dim	Crizzles.

Stones.

(*a*) *Batch Stones.* The most definite indication of a batch stone is the presence of minute quantities of gas surrounding the stones, their irregular form, and the excessive strain in the surrounding glass as seen when viewed by polarized light.

In many instances where the stone consists of more than one batch component, considerable quantities of gas will be observed, and there will be an appreciable difference in the refractive indices of the components. Quite frequently one meets with a condition where the stone consists of large quantities of sand or powdered silica, in which event the refractive index will be considerably lower than that of the glass. Felspars may be present in the sand, but these can be distinguished by their crystalline form, cleavage, refractive index and double refraction.

Occasionally one finds stones produced by large pieces of lime having passed through the furnace without being absorbed. Such stones have a snow-white appearance, are surrounded by considerable quantities of minute bubbles of gas, and often by

a pronounced strain with numerous striae radiating outwards into the glass. The immediately surrounding glass also will have a considerably higher index of refraction than the bulk of the specimen.

Batch stones consisting of an aggregation of all the components of the glass due to incomplete melting and insufficient temperatures are always accompanied by large quantities of seeds throughout the whole mass of the glass, and are completely surrounded by bubbles in close proximity to the stone; also the major portion of the stones will have a crystalline appearance with numerous striae radiating out into the glass. Because of the strain caused by most batch stones, minute checks or fractures will usually be observed if the stone is $\frac{1}{4}$ to $\frac{1}{8}$ of the thickness of the ware. If the ware is proportionately thicker, checks are not so likely to occur.

(*b*) *Clay Stones*. These are not always easily differentiated from certain types of batch stone, because much depends upon the period of time during which the stone has been in contact with the molten glass and the consequent degree of solution which has taken place. However, it is safe to assume generally that if the stone is more or less rounded, but of irregular form and not surrounded by bubbles, and if there are substantially no seeds or bubbles in the vicinity, the stone somewhat discoloured, and surrounded by a zone of a higher refractive index than the bulk of the glass, it is a clay stone, and probably has come from the disintegration of blocks, rings or pots. Further, clay stone when existing in a piece of ware will almost inevitably produce rupture, with small radiating checks, and although they may not be easily visible in transmitted light, they usually can be readily discerned with top illumination. Checks, however, are not always apparent in heavy ware, for if the stone is very small and exists in the centre of any section of heavy ware, the cooling from the molten to the solid state may take place slowly enough to avoid stresses sufficient to produce rupture.

Devitrification.

Probably 50 per cent. or more of the stones found in ware under modern methods of production are the result of devitrifica-

tion, and to the average work's operator, stones of this character are little different from any other stones. They usually result from long or repeated heatings at temperatures at which certain constituents of the glass crystallize out, or where, due to prolonged heating at a definite temperature, the whole mass of glass has commenced to crystallize. Personally, I make a distinction, for microscope study will usually reveal the difference between the two conditions, one being the crystallization of definite compounds, such as silica or silicates of lime, lead, etc. (which are readily recognised by their crystalline form and refractive index), and the other being the crystallization of the whole mass, usually in spherical form, beginning round a nucleus of some foreign substance and growing throughout the glass to an extent depending upon the temperatures, and the period during which the glass has been subjected to such temperatures.

CRYSTALLISATION.

Crystallisation might possibly be classed under the previous heading of Devitrification. However, I prefer to differentiate between them, for I consider that it is quite important to understand that devitrification is a crystallisation of the whole mass, while crystallisation considers the crystallising of definite chemical combinations of silicates, and I daresay that over 80 per cent. of "sandy glass," "rough glass," "white streak," "scum" and "hide" are caused by crystallisation of those components which exist in excess, or which, because of founding conditions, have not received the proper temperature treatment to bring them into stable chemical combination with the other components at the same rate as was effective on the constituents of the clear glass.

The numerous investigations made to determine the cause of this imperfection in feeders, and in the refining ends of tanks and in pots, show that in the majority of instances the chemical composition of a stone of this character approximates :—

Silica	83% — 85%
Calcium oxide	3% — 4%
Soda	11% — 12%

with varying amounts of aluminium, iron, etc. This stone can readily be identified in the microscope and especially in polarised light, for the major portion consists of crystals of tridymite, which has a very characteristic appearance. Further, the refractive index of this stone is usually considerably lower than that of devitrified glass or of clay stone, and but little or no striae will appear to radiate out from it.

While I have classed this condition under "stones," it is often spread out over considerable areas, because, due to the crystallisation occurring in the spout of the feeder on account of insufficient temperature and stagnation of flow, the crystals will be drawn down into the stream, and will, perhaps, form a band of an inch or more in width throughout the whole length of the article, depending, of course, upon the size of the article and the volume of glass forming the same.

Usually this crystallisation can be found on the surface of the glass in the feeder, furnace or pot. Occasionally, however, in the case of feeders, it will form at the orifice, or at a point where the temperature happens to be at the right degree to cause crystallisation. Under such conditions it is essential that a smaller orifice shall be used or a higher temperature maintained at the orifice; or finally the composition of the glass shall be changed so that the devitrification or crystallisation temperature shall be raised or lowered.

Salts.

Possibly I should have placed this under "crystals." However, as the conditions and characteristics are so different, I have differentiated between them. Stones arising from this cause are more frequently found in pots than in tanks, and are readily detected and identified by their crystalline structure, their high refractive index, and usually their low birefringence or isotropic properties, and can usually be definitely identified by grinding down the specimen until a thin layer of glass overlaps them, breaking this away and boiling in water, when the stone will dissolve. The crystallographic form may also often help to identify these stones, which consist of silicates, sulphates,

etc., of sodium. When large quantities of arsenic have been used, one occasionally finds a white stone caused by the condensation of arsenic, and this assumes the form of a blister, the interior of which is coated with arsenious oxide (which occurs as octahedral, monoclinic, or occasionally hexagonal crystals) or arsenic oxide (which is amorphous). Quite often, " glass gall," as it is called, becomes incorporated in the glass due to the early fusion of soda or potash salts. Such fused salts enter cavities in the pot caused by erosion, and are held there until the glass is worked down, or circulation has withdrawn the molten salts from these cavities and incorporated them in the glass. Under such conditions, these stones will appear in various forms, but rarely as spheres. More often they will be oblong or tadpole shaped, and when examined under the microscope, will have the appearance of a mass of cracked salt or possibly individual crystals. The glass immediately surrounding them will show a zone of striae, but few of these will radiate out into the body of the glass. These stones usually consist of sulphates or chlorides, but antimony, nitre, saltcake, soda-ash, pearl-ash, potash and all of the alkali salts are to be suspected where these stones exist.

Slacks.

The slack is a form of stone, the source of which I find has been very baffling to the average furnace operator. These stones exist only in tank furnaces. They may readily be identified by their composition, their position in the glass, their colour, and form. They will usually be found on the exterior of any article in which they are contained, will be oblong or tadpole in shape, and when existing in hand-gathered ware will be more or less spherical, or with a narrow tail when found in ware made by a flowing device.

Under the microscope, one will usually find a small white core in the centre. Petrographic methods of examination reveal that this white substance is usually sillimanite, and often radiating out from that, will be found minute crystals of tridymite and sillimanite. Therefore, it is obvious that the source of these stones is some clay material. The colour is very light brown,

deepening to jet black, and the size varies from $\frac{1}{4}$ to $\frac{3}{4}$-inch in diameter, being seldom less than $\frac{1}{4}$-inch. No seeds and few, if any, lines or striae are found surrounding the small core, except near the tail. However, the refractive index of the glass constituting the slack will be found to be approximately 1·6, or, at least, considerably higher than the clear glass surrounding it. These slacks are more prevalent in the old-fashioned tanks, where crowns composed of silica brick have been laid in a fire-clay mortar, or where ordinary sized bricks have been laid in channel and breast walls with fire-clay mortar—and especially in the old style furnace where the gas and air did not have an opportunity of mixing before they entered the furnace which, of necessity, created a reducing atmosphere, for it has been conclusively shown that these slacks are caused by the formation of carbon, silicon and aluminium compounds, which melt at a temperature higher than the working range of the glass. The obvious remedy is to eliminate all clay between silica bricks and the crown and side wall or, where this is not possible, one can alleviate the trouble and materially reduce the quantity of these slacks by regulating the fire so that the atmosphere within the furnace shall be oxidising in character. If these slacks are large and long, their source will probably be found at the breast wall and side walls of the furnace, near to the hole or the machine making the ware in which they occur. Excessive quantity of ash in the producer gas also forms slacks where no fire-clay mortar is used, but these are usually darker in colour, and contain numerous minute crystals of tridymite, and are most always found in furnaces fired by the old type of Siemen's producer, and having small gas checkers, and no middle damper.

Dim, Bloom, Clouding and Smudge.

In the early days of the Association there seemed to be much confusion regarding the causes and characteristics of imperfections occurring in glass subjected to reheating processes, and an attempt was made to obtain a definite nomenclature for these conditions. However, the committee dealing with this subject, never came to any final conclusion, and I therefore deal with the subject in my own way.

Dim. Dim is a semi-translucent effect which gives an appearance of opaqueness to transmitted light, and is entirely a surface effect. It is found almost entirely in the working of articles or tubing containing lead, and is a result of the reducing action or of the sulphur compounds of the flame upon the lead component of the glass. The appearance varies from a dark clouding to a deep brown or, in aggravated instances, a black colour, and often gives a mirror-like effect to the surface. It can be eliminated (so far as it is due to reduction) by a simple adjustment of the burners so that they give a completely oxidising flame. If, however, a considerable amount of sulphur exists in the gas, more accurate adjustment is necessary to obtain complete oxidation of the sulphur, in order to prevent the effect.

Devitrification also produces an opaque effect which is usually upon the surface only, and which can be classed as dim, although at times it has been found to penetrate some distance into the glass and, in more occasional instances, to have occurred within the body of the glass itself.

Bloom. This results from the presence of sulphur compounds in the gases, and can be entirely avoided if the gas be purified so that it contains not more than 0·02 per cent. of sulphur in any form. It has been found that the greater the quantity of potash in the glass, the more susceptible it is to the action of sulphur compounds. In soda glasses where no lead is present, the effect is a white coating which can be removed, to some extent by washing or dry polishing. However, the temperature at which the bloom is produced determines its stability, and when fairly high temperatures have been obtained over rather large areas, the bloom is stable, and is the result of a direct chemical action on the surface of the glass.

Clouding.

Clouding is a condition affecting the transparency of the glass, and is usually manifested as a white or opal coloured effect by transmitted light. Such a bloom may not appear when dry, but only when washed or wetted. It is a result of secondary heating of a glass containing fluorides, chlorides or sulphates,

whereby these constituents are transformed into what is apparently a colloidal form. This conclusion is arrived at from the fact that the effect can be produced only when the glass is submitted to a temperature slightly above the softening point over a given period of time, or where the glass is brought to a state which permits freedom of molecular arrangement, and it is presumed that under these conditions the electrolytes aggregate themselves into their colloidal form and consequently interfere with the transmission of light, the degree depending upon the size and quantity of such aggregations, and this determines whether the clouding has a white, opal or iridescent appearance by transmitted light.

At first it was presumed that dim and clouding both resulted from the same cause, but this was disproved when a long and laborious research was conducted to do away with dim and clouding by the purification of the gas. An apparatus was designed and put into operation which gave effective and satisfactory results in removing the sulphur compounds from town's gas to a point where dim was completely eliminated, the content for this condition being not more than ·02 per cent. of sulphur in any form. It was learned that this apparatus and the method used was the subject matter of a Patent held by Carpenter-Evans, and that some time after we had arrived at our conclusions an apparatus was put on the market by the South Metropolitan Gas Company, which effectively and satisfactorily removed such sulphur compounds.

During the course of this research we learned that bloom and clouding resulted from entirely different conditions. As stated, bloom was the result of a reaction between sulphur and the constituents of the glass at the surface, while clouding resulted from a precipitation or the formation of colloids throughout the whole mass of the glass. Therefore it is obvious that in lamp working it is first necessary to determine whether bloom or clouding is produced. If it is found that it is on the surface only and is a bloom, purification of gas is necessary. If, on the other hand, the clouding effect is produced throughout the entire thickness of the glass, it is the result of an excess of chlorides or sulphates.

In the fire polishing of tumblers, where dimming, bloom and smudging might all occur, it has been found that the addition of a small quantity of steam mixed with the gas and air assisted in preventing their formation.

Smudging.

Smudging is usually found on the surface of ware that has been subjected to lehr or annealing conditions, and results from the impingement of a flame containing carbon and nitrogen compounds. Smudging may be of two kinds: (1) a sooty coating, or (2) a white coating. In the first case, it is because of imperfect combustion resulting in the deposition of soot. In the second place it is caused by the formation of ammoniacal compounds which condense on either surface of the glass and form a white coating usually consisting of ammonium sulphates. Both of these surface deposits can readily be removed by washing.

Seeds and Blisters.

Numerous requests have been received from time to time, that we investigate the cause of seeds and blisters, and several of these investigations have been most interesting in character.

Seeds and blisters may be placed in four categories, for the source or cause of a blister is the same as that of a seed. Therefore we have air seeds or blisters, reboil seeds, batch seeds or blisters, and another which we may call a reaction seed or blister.

Air Seeds. We have found that the air seed or blister in hand operation is most usually caused by the method pursued by the operator in making the gather. To recite an instance: large blisters were found that invariably occurred in certain portions of the ware. After making an analysis of the content of the blister it was determined that it contained substantially nothing but air. Such analysis was conducted as follows.

A piece of glass tubing 5-10 mm. in length was cemented by balsam on the face of the glass. This section of tubing was filled with a solution of barium hydrate; by the use of a bow drill the glass was punctured, permitting the solution to flow

into the blister. No precipitation was observed. Therefore it denoted the absence of carbon dioxide or sulphur trioxide, which proved the absence of gases of combustion. Another blister was treated in a similar manner, a small quantity of aniline or other oil being introduced into the well and beneath this, by means of a hypodermic syringe an unoxidised solution of alkaline pyrogallol. The blister was punctured by a drill, or better still, a blow from a light hammer or a sharp instrument, thus permitting the solution of pyrogall to enter the blister. This solution immediately became coloured and darkened, thereby indicating the presence of oxygen. By these tests it was shown that the blisters were not occasioned by the evolution of gas from batch materials or extraneous matter residing in the glass near the point of gathering.

A careful study of the method of gathering soon revealed the cause of the trouble, for when the gatherer introduced his iron into the glass he made no attempt to rotate the stem and gather as would be the case in the forming of a goblet, but surged back and forth to a depth of three to four inches to obtain sufficient glass on the iron to form the article, with the consequent result that in making these repeated surges an overlap of the glass occurred entraining quantities of air which produced the blisters.

In another instance, numerous small blisters, as well as several larger ones, were found distributed throughout the entire article. Sometimes these had a slightly discoloured area and, where the blister had been elongated because of the blowing or stretching of the metal the narrow end, or tail of the blister showed straw colour or brownish tint. This occurred in one ring hole only, and upon analysing the contents it was found that there was but a slight trace of oxygen, and that the major portion of the content consisted of carbon dioxide. As the blister or seed occurred in one place only it was obvious that it could not be the result of chemical reaction in the batch materials, but must be due to the presence of some extraneous substance in close proximity to this ring hole. Proof of this was furnished when the furnace was let out, for it was found that immediately below this ring hole there was a piece of cast iron.

In other instances where similar conditions were observed, but where there was no discoloration of the blister, pipe heads, spanners, or other metallic substances were found at the bottom of the furnace. It is safe to assume that where large quantities of seeds and blisters are found in one definite or specific locality they are caused by reaction of the glass upon some foreign material. If the blister is of a straw colour, has little or no cloudy appearance, or the restricted end is dark brown, it is produced by the reaction of the glass upon cast iron, but if it is clear, with no clouding, it may arise from the presence of wrought iron, steel, etc. In one instance, a peculiar discoloration was observed, ranging from green to red, and it was found that this was caused by the presence of a small coil of copper wire.

Another instance which was rather baffling and which caused a great deal of discussion, was the presence of numerous small spherical seeds present in one place only. These were accompanied by minute areas which might be called stones. However, little or no opaque substance was observed as a nucleus to these aggregations, but under fairly high magnification in polarised light tridymite was found. This condition prevailed for some time but eventually it disappeared and, when the furnace was let out and an investigation of the blocks beneath the ring holes was made, it was found that there was a fairly large pocket in one block which had been formed by the erosive action of the glass and in the small indenture of the block, substantially pure sand was found. Therefore, it is presumed that during the forming of this block, through some agency, a quantity of sand had been introduced which resulted in the formation of these seeds and minute stones.

Reboil Seeds. We have had repeated calls to investigate and remedy the occurrence of some seeds of a spherical form. They occurred in large quantities in one or two instances, and could be observed in the parison before it entered the blow mould. They seemed to be millions in quantity but after the formation of the ware, and when it was cooled, few of them could be discerned by the unaided eye. When a section of this glass was placed under the microscope and observations made by oblique

or right angle illumination with a narrow beam of light, they could be seen in varying sizes and in large quantities. However, they were in all instances spherical in form and apparently had a fairly high refractive index. With this character of illumination the seeds were very bright and scintillating, while with direct illumination the smaller ones disappeared and the larger ones were opaque or black. This character of seed is almost certain to be the result of a reboil.

Possibly it would be well to define what I mean by the term "reboil." In tank furnace operation it often occurs that where perfectly plain glass is found in the melting end of the furnace, large quantities of seeds will be appearing in the glass that is gathered from the working end. Where such a condition prevails careful investigation will reveal either that the temperature of the working end (at the surface of the glass at least) is considerably higher than the temperature of the glass that passes through the bridge or, on the other hand, that at the bridge there is no reduction but rather a considerable increase in the temperature between the batch piles and the bridge, thereby maintaining an excessively high temperature and a continued reaction and solution of gases which, when the glass is cool, after passing through the bridge, become apparent in the form of minute seeds. It often occurs that proofs taken from the surface of the glass behind the bridge, and also at the working end will show complete absence of these seeds. If no skimming block is used at the mouth of the spout, there will be few or no seeds in the bottles or articles formed, but if the seeds are present they will usually be found at the backside (or the side nearest the tank) of the parison or the article formed therefrom. On the other hand, if a skimming block is used, and seeds are present, owing to excessively high temperature behind the bridge, the seeds will be found throughout the whole area of the article formed from any flow device.

If hand gathering be employed and seeds are produced by a continued high temperature behind the bridge, they will be found in zones or streaks in the ware, but if caused by excessively high temperature at the surface of the glass at the working end of the furnace, they will then be found throughout the whole

mass of glass. Also in the proof taken from the surface of the working end, but not from a proof taken from the surface behind the bridge, seeds produced from excessively high temperature in the melting end are usually more apparent in the parison than in the finished article, while those produced because of a reboil or excessive temperature at the surface of the glass at the working end are larger and fewer in number.

Batch Seeds. Batch seeds and blisters are the result of insufficient temperature or time in the founding period. That is to say, that for a given quantity of batch introduced into the furnace there are definite temperatures and time periods required to effect complete chemical combination of the constituents of which the glass is composed. I have heard it expressed that the melting of batch to make a homogeneous glass is a matter of temperature only, and I most completely disagree with this view, for irrespective of how high a temperature may be obtained, a certain time period is required whereby chemical reaction can take place between the constituents in order that homogeneous or perfect glass can be made. I have often found that the designers of tank furnaces have overlooked this very important factor, and that an excessive temperature has been maintained requiring an excessive amount of fuel and poor economy, because the length of the furnace or the time that the batch can reside in an atmosphere of the required temperature has been greatly in excess of the normal and consequently an excess of temperature has been obtained and unnecessary quantity of fuel used. Or to put it the other way, in a furnace which is considerably longer than it is wide, and which is called upon to melt only about one-half to two-thirds of the normal amount of its melting capacity, the temperature employed could be reduced 50° or 100°, with a consequent reduction in fuel consumption, and equally good glass could be produced. For, while there is a minimum temperature at which satisfactory chemical reaction takes place, and as there is a normal or efficiency temperature of melting and founding, any temperature in excess of this, with a required length of furnace which will permit of a sufficient time period whereby full chemical reaction can take place, causes an expenditure of fuel which is a waste. Several

instances can be cited, as in one case, with the furnace approximately 15-feet in width and 28-feet in length, an average temperature of 1460° was maintained while the demand upon the furnace seldom exceeded 16 tons per day, or less than one-half of its capacity. The result was that it was seldom that one found a batch pile beyond the second port, or 15-feet down the furnace. Therefore there was substantially 15-feet of the melting end which performed no useful function but, on the contrary, caused a great loss in fuel. In other words, this furnace was capable of producing substantially 30 tons of glass per day without any additional fuel consumption. On the other hand a furnace 20-feet in width and 18-feet in length operating at the same temperature, required very careful adjustment and operation to prevent the production of batch seeds and stones. In the first instance, the temperature was reduced to between 1380° and 1400°, and equally good results were obtained, with approximately a 12 per cent. saving in fuel. In the second instance it required the application of draught on the furnace and pressure on the producers to obtain sufficiently accurate control to ensure the absence of seeds and uniform properties of the glass. This perhaps was augumented by the lack of sufficient chimney draught in the 20-feet furnace, for the height of the chimney above the ports was but about 55-feet, while in the first instance the height of the chimney was approximately 65-feet above the ports.

In the first instance batch seeds or stones were seldom found, while in the second one, the greatest annoyance and possibly the cause of the greatest loss of ware was due to these factors.

Seeds and blisters occurring in ware made by the Owen's machine may be produced by any of the above causes, and in addition, there are three other sources. (1) If the stream of glass is wide, and not uniform in temperature, and thickness, or does not fall into the revolving pot at a true 90° to the radial line, a fold or lapping may occur that entrains air. (2) The cut-off may occur in such a manner as to enfold air. (3) Imperfect combustion of gas or oil may entrain particles of carbon or ash and produce a blister or seed. These can be distinguished by the fact that when seen in the hot parison they have a dark

or brownish boundary line, and are usually spherical, while an air seed or blister is clear and usually larger.

CORDS.

Considerable work has been done on cords to determine the cause of and remedy for various characters of cords. However, I think that the principles involved in the detection and determination of cords may be found in Bulletins 1 and 2.

In tank furnace operation probably the greatest source of cords is changes of temperature, and the major portion of the cords existing in ware arise from varying viscosity in the different areas of the glass, due to changes of temperature. Therefore the remedy naturally is to supply and utilise means of obtaining more constant and uniform furnace regulation of the melting, refining, and working end temperatures.

Where cords exist which are caused by a lack of uniformity in the composition of the glass, they are usually attributable to lack of uniformity in founding conditions and again indicate a lack of proper temperature control. Small cords and strings that are caused by solution of blocks, rings or refractory material are readily distinguished from the others, and the obvious remedy there is to obtain a better grade of refractory or to apply cooling in order to lessen the rate of solution of the refractories.

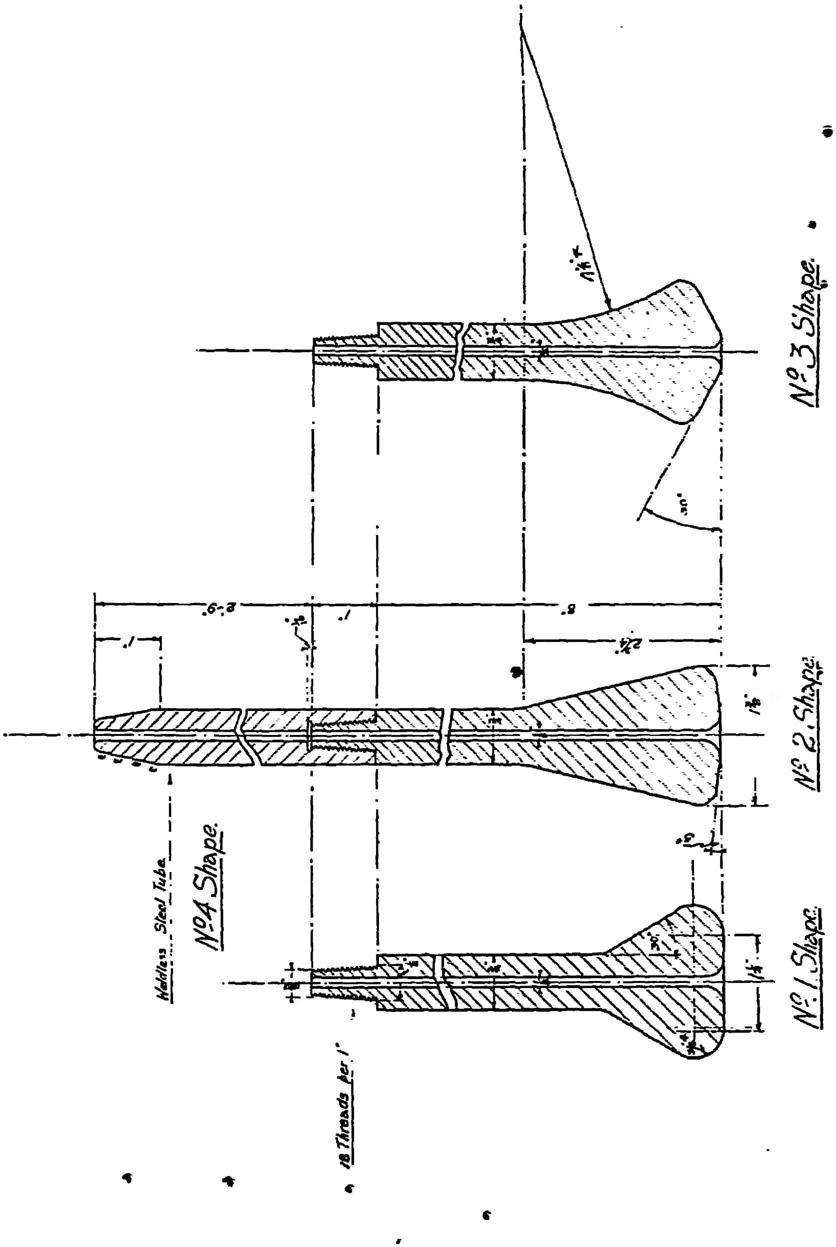
CHECKS AND CRIZZLES.

These are usually the greatest enemy of the automatic machine operator. Because of the varying conditions under which they occur as well as their varying appearance, their causes and source become somewhat confused, especially to one who has not had previous experience with machine operation. As an instance, more than 50 per cent. of the ware of a certain plant was being thrown away because of checks in the rings of pickle bottles. A careful study of these checks showed that the great majority of them occurred at a definite spot in the ring and that they were about $\frac{3}{16}$-inch from the mould part mark. The cause of these checks was attributed to everything from the composition of the glass to the lehr, but it was pointed out, that the lehr or batch must have human intelligence to

produce these checks at an identical spot each time. An investigation of the moulds used, when cold, revealed no cause, but careful measurement of the mould when hot proved that it had become distorted and that the dimensions across the body were less by 3/1000 to 4/1000-inch, than the opposite diameter, with the result that, as the moulds opened, a slight pinching effect occurred which fractured the nearly solid skin formed at this point. Checks resulting from such a cause would be vertical. Again, checks on the interior which are vertical or at a slight angle from the vertical would be produced by the movement of the plunger in a lateral direction or canted slightly at the instant of its removal. Horizontal checks occurring on the exterior were found to be due to the rocking of the ring mould upon the parison mould at the instance of the opening of the parison mould. Checks are often caused at the shoulder or in the neck upon certain machines, especially in large ware where too rapid transfer is made which, due to the inertia of the heavy parison, suspended from the neck, causes a check to occur just below the ring mould. This can be remedied by slowing the transfer. Occasionally checks are found in the bottom and these are almost invariably caused by the bottle being placed on a cold surface.

PIPES.

Investigations made in the factories of members concerning the form, shape and use of blow pipes, led to a search for a metal or a treatment of pipes whereby the moils would be substantially free from scale. Several kinds of alloys were tried, most of them being of a nickel-iron mixture, and those gave very good results. However, the cost of these, and the difficulty of adapting the heads to the barrels and maintaining a tight joint does not make this form of pipe all that could be desired. Ordinary iron pipes were then treated for a length of about 6-inches to a calorising process, that is, the impregnation of the metal with aluminium which prevented oxidation of the iron and eliminated practically all the metal from the moils. These pipes have given good satisfaction, and if they are used there is no reason why moils should be discarded even in the making of the highest class of lead flint.


No. 3 Shape.
No. 2 Shape.
No. 1 Shape.
No. 4 Shape.
Weldless Steel Tube
18 Threads per 1"

Heretofore the presence of considerable quantities of iron scale remaining on the moil has been the source of a considerable loss of glass, particularly so where the better class of tableware is being made. It was noted that the shape of the pipe used in most of the factories in England is such that the operator invariably takes up about two or three times the amount of glass that is required to produce a moil or attach the article to the pipe-head. Hoping to do away with this, I introduced into two or three factories, a shape of pipe that is being used in the United States, and where the moil in the forming of 6, 8 or 10 oz. glasses should not amount to more than ½-oz. Again we found some difficulty in getting these pipes adopted for the reason that the workmen objected to changing their procedure. The diagram attached shows several forms of these pipes, No. 3 being the more prevalent one for all kinds of light ware, from liqueur glasses up to 10-oz. beers, while Nos. 1 and 2 are used for heavier ware. This subject is one upon which manufacturers could not make any mistake in undertaking a little experimental work, and following it up, especially with the calorised pipes, for it is only necessary for them to ship a set of pipes to the Scarab Oil Burning Co., Ltd., c/o International Paint and Composition Co., Ltd., Felling-on-Tyne.

ANNEALING.

Our investigations into the subject of annealing have been wide and varied, and to give a comprehensive review of all our activities in this direction would be more voluminous than this summary could bear. Therefore I will deal with the more distinct difficulties and problems and relate them to the causes and remedies in as brief and concise a manner as possible. I will place the ware to be considered from this standpoint in seven classes :—

Lamp-worked and scientific apparatus.
Chemical glassware.
Miners' lamp glasses and heat resistance ware.
Electric light bulbs.
Table-ware.
Sheet and plate glass.
Bottles.

The annealing of articles in each of these classes must be considered from two distinctly different viewpoints, so far as the requirements affecting annealing are concerned, *i.e.*, hand or automatic machine made. In the first three, or possibly four classes the method of manufacture does not have as pronounced an effect upon the annealing requirements as in the succeeding classes. However, I think that the general principles governing annealing must receive separate consideration, even in the first three classes although possibly it is a matter of degree only. By this, I mean that where ware is produced by hand, a greater period of time elapses between the gathering of the glass from the molten state to the time when it is subjected to any annealing operation and, as a consequence, a greater quantity of initial heat is lost, and therefore the reheating for annealing must require a greater period of time, but possibly no greater temperature. The annealing process therefore should be designed and operated accordingly, which means that a lehr which might be correct in design and operation for light blown chemical-ware would not give satisfactory results for table-ware or bottles.

But little investigation has been made concerning the best type of lehr to be used in annealing lamp-blown or light chemical ware, for it would seem that when properly constructed and operated, the lehr and annealing process as designed by Whatmough is quite satisfactory. The principle upon which this lehr operates is without doubt correct, and if properly constructed and adjusted there is no reason why ware of approximately the same thickness and weight cannot be thoroughly annealed so that all strains detrimental to its use shall be completely eliminated.

The annealing of light blown chemical glassware such as beakers, flasks, etc., is a comparatively simply and easy matter in comparison with the heavier classes of ware, such as tableware, and bottles, for while it is still a moot question as to what degree of annealing is required to obtain the best physical condition of the glass to withstand changes of temperature when used in the laboratory, yet I think it is generally agreed that the annealing required is of a character which will relieve all stresses in that particular piece of ware, which have occurred in forming. These

are set up in the rings, edges, joints, etc.; or where there is a considerable difference in the thickness of the glass, and as it is necessary to regulate the temperature and time so that the annealing process shall be effective upon the heavier sections, it is obvious that the lighter ones will have all of the stresses removed.

A case in point is lamp bulbs. The only reason for annealing these at all is to facilitate and ensure safety in cracking-off the neck of the bulbs. As the neck is the heavier section, it is only necessary to pass the bulb through the heating chamber so that the heavier section is brought to a temperature which will permit of complete molecular readjustment. The latest method of accomplishing this result is by passing the bulb through a tube heated electrically or by gas, to the required temperature. In miners' lamp glasses, gas globes, etc., investigation shows that if these be manufactured under conditions that will produce uniform stresses, no annealing is required. In fact, if the shape and character of the article are such as to enable one to augment the stresses on the interior so as to be in excess of those existing on the exterior of the article, a more satisfactory heat resisting piece will be produced, for the reason that sudden changes of temperature in the interior due to contact with flame or the sudden application of heat operate to relieve these stresses. On the other hand, if the article has been thoroughly annealed the impingement of flame or the sudden introduction of temperature will produce a stress which, because of the sudden expansion of the interior, will produce a high tension strain on the exterior and, in consequence, tend to rupture the piece, and obviously the greater the thickness the greater the danger of rupture. In Welsbach globes, and Argand and ordinary lamp chimneys, the latter methods require the application of special means of cooling, producing excessive, but uniform cooling of the interior of the article, and as the ware is comparatively thin the stresses so produced extend practically into the entire thickness of the article. This is equivalent to the so-called hardening or tempering process used by the Germans on chemical ware, gauge glasses, etc. One of the methods which has been successfully applied to the making of Welsbach globes, lamp chimneys, etc., is to pass into the interior of the globe or chimney immedi-

ately after blowing has occurred, a highly humid atmosphere which because of its increased heat carrying capacity, effects uniform and rapid cooling. Such articles are better left unannealed.

Investigations made in a number of factories clearly indicate that the principles of annealing have received but little consideration, and this is especially true in table-ware and bottles. As an instance, when an exploration of the temperature of a lehr was made, it was found that in the heating chamber the temperature of the pans upon which the ware rested was barely 250° C., while the temperature at the top of the ware was approximately 500° C.; at the discharge end of the heating chamber the temperature of the pans due to the contact of the hot ware, and to the radiated heat, rose to approximately 400° C., while at the tops the temperature remained at approximately 500° C. However, as soon as the ware passed out of the heating chamber the draught produced by the chimney and the opening at the discharge end brought the temperature of the pans down to less than 100° C., but at the top of the ware the temperature was approximately 400° C., while within the next 6-feet, the temperature of the atmosphere at the top of the ware dropped to 250° C., and at the pans approximately 70° C., so at the discharge end of the lehr the ware was practically at atmospheric temperature.

Obviously such conditions as these induce excessive breakage. The remedies were to enclose the chimneys entirely, place an asbestos cord curtain from the crown of the lehr so that it barely escaped the tops of the ware, to close up the opening underneath the pans, to prevent any circulation of air through the length of the lehr, and to introduce gas burners into the heating chamber underneath the pans and raise the temperature to a required degree, *i.e.*, between 400 and 500° C. This procedure reduced the breakage on the lehr from about 50 per cent. to between 2 and 3 per cent.

This lehr was of the open fire type, heated by producer gas and in all such types of lehr, combustion takes place in the heating chamber, and the temperature over the area of the chamber, varies to a considerable degree. It was found that in the

middle and at the top of the ware a temperature of 510 to 520° C. could be obtained while, at one side, and at about the middle, a temperature of over 600° C. was found, and on the opposite side the temperature was about 450° C. This illustrates the wide variation that is possible in lehrs of this type. Further, as such temperature is obtained by convexion or direct heating by combustion, it is almost impossible to prevent excessive local temperatures being produced, but this does not mean that the necessary heat is all available for heating the entire mass of ware to the required temperature, for it is possible that when the piece occupies one position, it may receive the required treatment, but immediately it is moved into another position, the temperature is changed, and so on, until possibly and quite likely, there are portions of the ware which have not received sufficient temperature to obtain the relief of the stresses.

From all investigations made on this type of lehr, I can only draw the conclusion that it is absolutely essential that the temperature underneath the pan should equalise that above the pan, and that the fire both above and below the pan shall be susceptible to control to a degree that will enable one to obtain the required temperatures throughout the whole area of the heating chamber. This is a rather difficult matter, and for that reason I advocate the muffle type of lehr, particularly for the annealing of table-ware and bottles.

ACID POLISHING.

Investigations made into acid polishing show that it is almost impossible to lay down any definite and predetermined procedure or formula for an acid polishing solution, because the composition of the glass and its physical properties have much to do with the efficiency of acid polishing, and it was shown that where in one instance, very good results could be obtained by using 30 per cent. acid making three dips, another glass of supposedly the same composition, but actually being slightly higher in lead and alkalies, required five or six dips, with a much stronger acid.

It was also found that in some instances much better results could be obtained by first dipping in 12 per cent. sulphuric acid, and then making two or three dips in a 30 per cent. hydrofluoric acid, the temperature of the latter being maintained at from 30 to 35° C.

It was also found that washing the ware with ordinary tap water which was high in lime produced an inferior polish to that obtained when the ware was washed or rinsed in rain or distilled water before being put into the acid solution.

Probably the greatest difficulty in obtaining good acid polish is the variation in the strength of the hydrofluoric acid on the market. Investigation was made concerning the strength and purity of acids, and a wide variation was found. Orders were placed for commercial hydrofluoric acid 50 per cent. strength, and the variation in different samples obtained from time to time ranged from 60 per cent. to as low as 38 per cent. hydrofluoric acid, with from 0·6 per cent. to 4·0 per cent. hydrofluosilicic acid and with sulphuric acid from a bare trace to as high as 8 per cent.

It is obvious that with an acid polishing solution made from a given formula and using acid that varies as widely as shown above, it is impossible to obtain anything like uniform results without determining the actual acid value. The following formula and procedure for ordinary types of lead glass containing from 25 to 30 per cent. lead gives excellent results. The ware is first dipped and brushed in a solution of 12 per cent. sulphuric acid, and is then dipped into a solution made up as follows :—

HF (50 per cent.)	2 parts
H_2O	1 part
H_2SO_4 (Sp. gr. 1·8)	1 part

This solution is best made up by slowly adding sulphuric acid to the water with constant stirring and, after it is cool, adding hydrofluoric acid with constant stirring. The solution should be kept at 30-35° C. during its use. The best results were obtained by repeated dipping and brushing with a rubber brush. After the ware had been dipped in No. 2 solution until sufficient polish was obtained a final dip was made in a No. 3 solution consisting of approximately 20 per cent. sulphuric acid, and lastly in water, thoroughly rinsing and drying.

BADGING.

In the beginning of our activities we were called upon to investigate the process of badging. While numerous processes were in use which demanded application of heat and rather accurate procedure, in order to produce clear, distinct and effective badging of more or less intricate and fine design, none were capable of being applied by means of a stamp, stencil or similar means. After considerable experiment, a compound was evolved which, according to the reports of the users, gave very good results. This compound consisted of the following :—

Glacial phosphoric acid (Sp. gr. 1·7)	10 parts
Water	1 part
Ammonium fluoride	1 part
Zinc oxide	2 parts
Copper chloride	1/20 part

The zinc oxide is mixed with the phosphoric acid, the latter being at a temperature of about 60 to 70° C., the two being thoroughly mixed in a mortar or mill; to this is then added a few drops of saturated solution of potassium dichromate and copper chloride. The ammonium fluoride is dissolved in the water and, just before using, the phosphoric acid paste and the ammonium fluoride solution are mixed together, spread upon a rubber pad and distributed by means of an inking roller. This is then used with a rubber stamp in the ordinary manner. If possible it is well to have the article to be badged at a fairly high temperature, *i.e.*, 60-70° C., in order to hasten the reaction; after this has been effected the article is set aside for several hours, when any residue is wiped off. Another method is to make a paste consisting of :—

100 parts dextrin
10 parts finely powdered graphite
20 parts ammonium fluoride
20 parts sodium fluoride.

These are made into a paste with just enough hydrofluoric acid (58-60 per cent.) to give a consistency of putty. This paste can be used either with a stencil direct upon the glassware, or it can be stencilled upon paper and then used as a transfer. If a considerable number of transfers are made up and used

from time to time, it is as well to moisten the transfer with 10 per cent. sulphuric acid solution, apply to the article and allow to stand for several minutes, after which the paper is removed. After standing for a further 15 mins., the article is cleaned and it will be found that a frosted etching has taken place.

The colour of the badging can be altered by utilising different forms of pigment, *e.g.*, ferrous carbonate for brown, ultramarine for blue, red lead for brownish or brick red, and cadmium sulphide for yellow.

LIME.

During our original factory investigation it was found that there was great confusion concerning the meaning of the various terms applied to lime in its different forms, and in order that we might accurately determine the nomenclature for lime, we obtained, from nearly all members, specimens of the lime which they were using, the name under which it was purchased, and also the name which they gave to it. The result of this enquiry shows that many glass makers are ignorant of the materials which they are using. I therefore suggest that both the suppliers of limestone and the glass manufacturers arrive at a definite nomenclature for their products, and that the glass manufacturers in purchasing their lime, shall do so under specification and under the proper name, *e.g.*, if limestone is used or purchased, that it be purchased as limestone, and not as limespar or calkspar. If manufacturers will give this their attention and insist upon a definite nomenclature being used, it may at some time or other, relieve them of serious difficulties, for I have found two instances, where, because of inability to obtain supplies of one class of material from one firm, a manufacturer ordered it under the same name from another firm. A different class of material was sent and used, resulting in heavy losses.

ELECTRICAL CONDUCTIVITY.

During the last year much time, labour and money have been spent upon researches into the electrical conductivity of glasses, and although the investigations made on glasses at

low temperatures revealed some peculiar phenomena and interesting results, they were not of a character whereby the results could immediately be translated into factory practice. The true motive behind this investigation, at least so far as I was concerned, was to determine if electrical conductivity bore a definite and constant relation to the viscosity of glasses at working temperatures, and as all of our experiments with glasses of ordinary commercial composition indicated that, with but few exceptions this was so, and as those exceptions occurred over varying limits of variability of temperature it did look promising, and I think it is possible to utilise the property of electrical conductivity to determine the viscosity or the characteristics of the glass in the making of any form of glass article, where such forming is of automatic nature.

Mr. Bryson has had this research in charge, and his work has been very thorough, and I believe that the electrical conductivity curves obtained supply adequate proof that a thorough and careful investigation of the electrical conductivity of glass at working temperatures is warranted, particularly in cases of flow feeds and automatic feeding operations. Some of the results of this work appear in the bulletin, but up to the time of writing we have not yet sufficient data of absolute viscosity measurements, electrical conductivity or surface tension to enable us to set down specific and definite conclusions that will relate conductivity to any of the other factors.

It is well known by those who are skilled in the operation of automatic flow devices, press and blow operations, sheet, cane and tube drawing, that it frequently occurs that, at certain temperatures the viscosity and surface tension do not follow, or are not in strict accord with, the theoretical curve, but it has been found that the curves drawn from electrical conductivity measurements were more closely related to the working properties of the glass than could be deduced from measurements of temperature, viscosity or surface tension alone.

Bearing these results and conclusions in mind, I felt and still feel, that it is only a matter of applying the proper apparatus and learning the method to be pursued in operating such appara-

tus, to evolve an equipment, which from the operator's standpoint, may be of inestimable value. While it would be very desirable for one to be able to relate these four factors in absolute numbers and indices, it is not necessary. Nor do I believe that in many instances would it be advisable to use the absolute numbers or indices for, after all is said and done, with the highest degree of accuracy in the method of measurement, the operator is really concerned only with changes in the properties of the glass with which he is working, and requires only a sufficiently accurate but pronounced effect to enable him to make such necessary adjustments as regards those factors that control the weight of glass to be delivered to the forming apparatus.

Working upon this basis, we installed an apparatus into a flow spout of the Hartford Fairmont Feeder and while some results were obtained that indicated the soundness of our theory, we were so unfortunate as to have all of the elements put out of commission before sufficient data had been obtained to warrant our adopting that particular form of arrangement of apparatus as a commercial proposition. However, from the results which were obtained, I am fully convinced that a careful study of this principle should be made, and as a result of the knowledge gained therefrom, an apparatus could be evolved that would meet with the requirements, thereby accomplishing that which would be of enormous benefit to the glass manufacturer.

REFRACTORIES.

The extensive research that was commenced at Stourbridge on the compounding, forming and burning of tank blocks is not yet completed, and a great deal of the value of this research will evolve from relating those blocks fired in direct-fired kilns with those burnt in a gas-fired kiln, also from clays which have been soured for only a few weeks compared with clays that have been soured and pugged once a month for a year.

I believe the results that have already been obtained upon refractories, indicate that porosity alone is no criterion upon which to determine the efficiency of a tank block. It does seem quite evident that the presence of considerable free silica

and high silica content in the clay are sometimes advantageous, but a great deal depends upon the physical properties of the fireclay used.

Another matter which I think is of vital importance for the Association to determine, is the method of burning, for it is quite obvious to me that many thousands of pounds have been lost, and the characteristics of what would otherwise have been good refractory materials, have been ruined in the kiln during the burning. This has been caused, partly by the fusion of ash upon the block, thereby causing spalling and other imperfections, and partly by the absorption of kiln gases, mainly during the prolonged holds which are customary. It appears that in order to obtain blocks burned to a satisfactory temperature, a new method of firing must be employed which probably will ultimately depend upon oil or producer-fired kilns.

During my visits to the numerous plants using pot furnaces, I invariably heard the complaint that the siege and the eye of the furnace were the cause of the major portion of the troubles, the eye eroding in an irregular manner causing some pots in the furnace to become useless owing to the high impinging action of the flame. Upon investigation, I learned that nearly all sieges were constructed of blocks formed of refractory clays, but that the composition, formation and burning were very uncertain. Even where a siege had been ordered, and the blocks were on hand, it was found that there was a wide variation in the density and texture of the blocks. It therefore appeared that much could be done to relieve the troubles of the furnace operator if a siege having more uniform characteristics could be devised.

During our investigations on refractories we had occasion to experiment with various mixtures for the purpose of forming tank blocks, and when building an experimental furnace in the laboratory, certain of these mixtures were used, with the idea of obtaining some preliminary information concerning their properties, with the result that one mixture gave such excellent results that it was decided to apply it to the siege of pot furnaces. At the factory of one of our members a siege of this material was placed, being laid *in situ*. After nine months of operation

s siege showed no deterioration whatsoever, and the eye of : furnace has suffered no erosion or abrasion. This result, hink, should be considered by all members using pot furnaces, : it is not necessary to make this material into any shape, the ocedure being as follows :—

Siege mixture No. 3, the formula for which is in the records the Association, is wetted until it will just hold together when thered in the hand (this corresponds to a moisture content about 11 per cent.) The old siege is removed to a depth of ›out five inches, and a wooden form is fixed so as to give the ıape of the eye, the material being at least eight inches thick at ıe lip. The mixture is then put in to a depth of two or three .ches, and stamped down, until it appears to be solid. Additional ›rtions are then applied and the stamping continued until the ege is built up to the required height. After it has been com-leted,the surface is wetted slightly and sillimanite, ground to pass 0 mesh and mixed with 5-10 per cent. of ball clay is trowelled over ıe surface to a depth of ½-inch. This is allowed to dry for two or ıree days, after which a slow bucket fire is placed in the eye or ›ell of the furnace, the furnace being closed so that a very slow .rying fire is being carried on for two or three days, after which t is gradually increased until a temperature of approximately !00° C. is obtained within the furnace. It is then opened up, ıllowed to cool and any shrinkage cracks which have occured ıre then filled up with surfacing mixture, after which the usual ıeating up fires are applied. Just before setting the pots, the siege s covered with sand in the usual manner.

In the furnace above referred to, several pots had broken, ınd the glass had run over the siege and down through the :ye, but it had no effect whatsoever upon the material, in fact, it ıppeared as if the glass did not wet the sillimanite, and therefore lid not adhere to it. This is also shown by the fact that in remov-ng the broken pots, no difficulty whatever was experienced by :heir sticking to the siege, and they came away without any :ffort.

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ERRATA.

Bulletin 2.—Page 51, line 18, *for* " 1,700 to 1,900 " *read* " 17,000 to 19,000."

,, 6.— ,, 21, line 1, *for* " pro-duce " *read* " produced."

,, 6.— ,, 23, line 6, *for* " distant " *read* " distinct."

,, 6.— ,, 41, line 5, *for* " TcO_2 " *read* " TiO_2."

,, 6.— ,, 41, heading of column 5, *for* "meterial" *read* " material."

,, 10.— ,, 42, line 7 from bottom, *for* " Read " *read* " Red."

,, 11.— ,, 17, heading of Table IX., *for* " Batches containing Sodium Nitrate " *read* " Batches containing Carbon."

,, 12.— ,, 15, line 7 from bottom, *for* " O " *read* " Q."

,, 12.— ,, 79, line 10, *for* " unprotected " *read* " unaffected."